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VOL. XXIII, No. 6 June, 1953

In This Issue

Crimping of Wool Fibers
M. Horio and T. Kondo 373

The Heterogeneity of the Keratin Fibers
E. H. Mercer 388

Relation Between Dyeing Properties of Wool and Modifications of the Fiber
Gösta Lagermalm, Joel Lindberg, and Leonard Weissbein 398

The Analysis of Cotton-Glass-Asbestos Yarn
Clifford L. Hilton 401

The Tensile Behavior of Some Protein Fibers
G. Susich and W. Zagieboylo 405

A Study of Soiling and Soil Retention in Textile Fibers
The Effect of Yarn and Fabric Structure in Soil Retention
W. J. Hart and Jack Compton 418

A Two-Dimensional Load-Extension Tester for Woven Fabrics
C. H. Reichardt, H. K. Woo, and D. J. Montgomery 424

Further Studies on Cotton Cellulose with Reduced Crystallinity
Leon Segal, Mary L. Nelson, and Carl M. Conrad 428

Letters to the Editor
Effects of Ultrasonic Radiation on the Viscosity of Cellulose Solutions 436
The Determination of Nep Counts 437
The Shearing of Filaments and Yarns 438
The Allwörden Reaction 440

Book Reviews 442

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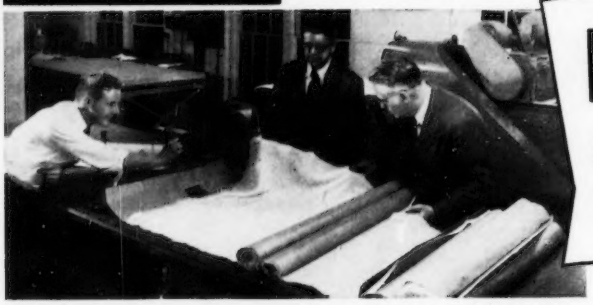

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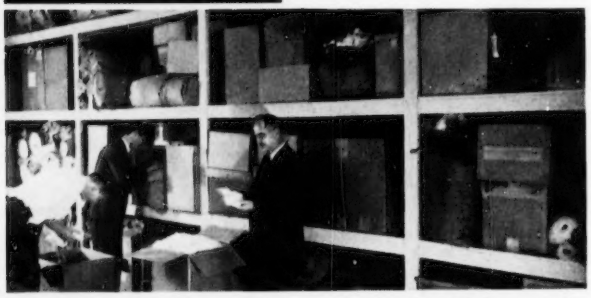

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TEXTILE RESEARCH JOURNAL

VOL. XXIII, No. 6 June, 1953

Crimping of Wool Fibers

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Abstract

By employing differential staining under controlled conditions and by experiments on resistance to chemicals, it is shown that wool possesses an inherent bilateral structure which runs the entire length of the fiber from root to tip. The similarity in behavior of wool, as shown in this study, to the formation of crimp in viscose rayon indicates that structural asymmetry may be responsible for the coiling and crimping nature of the wool fiber. Isolated single wool fibers show a pronounced tendency to coil; however, when movement is restricted by the proximity of other fibers in a lock or in mass, the result is the formation of crimp.

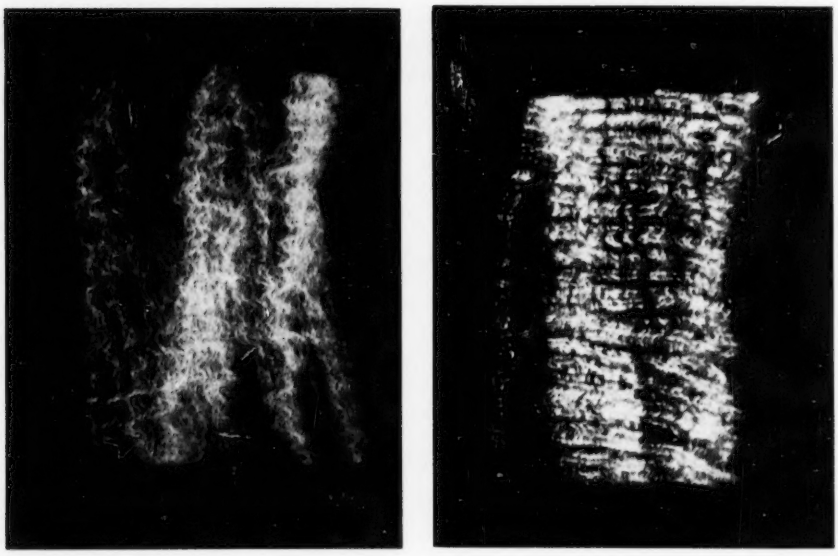
THE unique and highly esteemed status of wool in textile fields is due largely to its excellent crimp, which is a basic characteristic of wool fibers. In view of its practical importance, research workers in various fields of science and industry have long been interested in crimp. In this paper it is intended to provide further information concerning the crimping of wool fibers and the mechanism of crimp formation.

In a previous paper on crimped rayon staple [5] it was shown that the filaments which produce crimps have a marked tendency to coil owing to their bilateral structure, and it was discussed how significantly this coiling property of each individual filament functions in producing crimps of the filament bundle. The analysis of this dominant feature of the mechanism of producing crimps in rayon staple has induced us to extend the study to determine whether or not an analogy can be found in crimped animal hairs, especially in wool fibers, because of a close resemblance in the appearance of the crimps (see Figure 1 (a and b)).

The matters treated in this paper are confined to the results of observations obtained by applying methods similar to those described in the previous paper. The results of the present study indicate that an exactly analogous structure exists in both kinds of fibers—namely, wool fibers also seem to be bilaterally constructed in such a regular manner as to be correlated with their coiling and crimping. For the convenience of reference to the previous paper, the present discussion will follow in general the same sequence.

Bilateral Structure of Wool Fibers

Filaments of crimped rayon staple could be characterized by an asymmetric cross section which is smooth and thick-skinned on one side, but deeply indented and thin-skinned on the other side (see Figure 4 (a and b) of the previous paper). This apparent asymmetry of the cross section indicates an asymmetry of the inner structure. Owing to the dif-



a b

FIG. 1. *Crimps of wool* (a) *and rayon fibers* (b) *(magnification, 3 ×).*

ferent mechanical responses of the two structures, each single filament has a pronounced tendency to coil. A significant point is that the smooth and thick-skinned side always faces towards the inside of curvature. This coiling property was analyzed in detail, and was shown to be the original motive force for producing the crimps.

Evidence that wool fibers also are constructed bilaterally throughout the entire length of fibers would indicate that an analogy exists between the two kinds of fibers. An analysis of the shape of cross sections of wool fibers does not offer any distinct evidence of bilateral structure, since the cross sections of wool hairs are, in general, oval or circular. However, there are several indications that wool fibers also are heterogeneous in structure.

Notable observations were made by Ohara [6], who found that the fibers of Merino wools of three different species are only partially stained by the buffered solutions of several basic dyes and showed that the outside of curvature is stained a darker tone than the inside. It is also known that the bilateral structure of wool fibers can be revealed by the difference in the resistance to chemicals [3]. Thus far, however, these observations have not been correlated with the coiling and crimping nature of hairs.

The partial-staining method as presented by Ohara

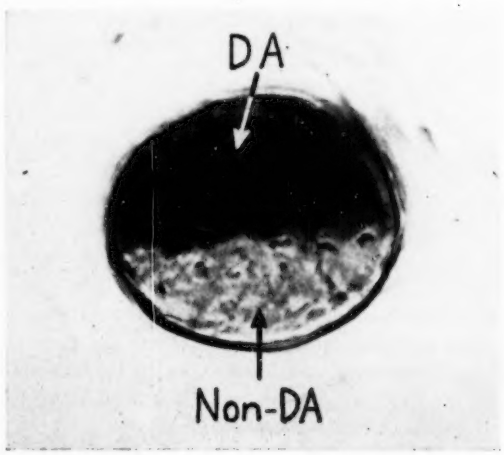
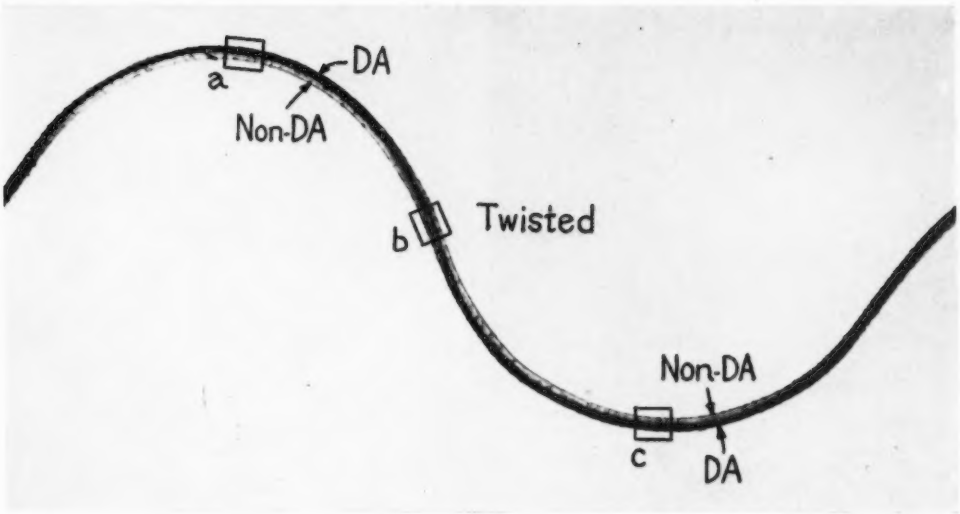


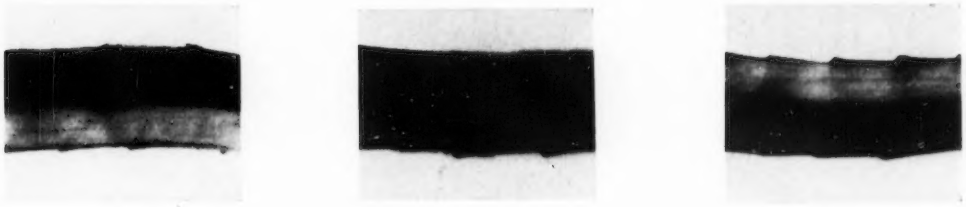
FIG. 2. *Differentially stained cross section of a wool fiber (magnification, 1500 ×). The dye used was Janus Green.* DA—*Dye-accessible.* non-DA—*Non-dye-accessible.*

was found to be very useful to reveal the structural asymmetry of wool fibers, which can be correlated with their coiling and crimping nature. The method was modified, and it was found that washing the fibers with a very dilute acid immediately after staining enhances the contrast of color density.* Of sev-

* See the section on experimental procedure (p. 385).



(*Magnification, 100 ×*)



a (*700 ×*) b (*700 ×*) c (*700 ×*)

FIG. 3. *Part of a wool fiber stained differentially by Janus Green.* Non-DA *always faces towards the inside of curvature, and* DA *towards the outside of curvature. Notice the diagonal twist between the maximum and minimum points of waves.*

eral basic dyes which effected the partial staining of wool fibers, Janus Green was found to be the best for this purpose. Differential staining occurs whether the fibers are stained in the form of flock or stained after sectioning.

Figure 2 shows a partially stained cross section of a Merino wool fiber. For the convenience of description, the portion stained in the darker tone is labelled "DA" (dye-accessible), while the lighter part is labelled "non-DA" (non-dye-accessible).

The partial staining of wool fibers is not new. Royer and Millson [9] presented a variety of cases of partial staining which are of importance in the field of wool dyeing. However, the significant point is that the differential staining as obtained by this method can be used for interpreting the coiling nature of wool fibers.

The most significant point in connection with the crimping nature of wool fiber is, after all, the regular orientation of cross sections, as was the case for the crimped rayon staple. When DA and non-DA are traced along the entire length of a crimped wool fiber, it is recognized that the rule is applicable to wool hairs also. In Figure 3 is shown part of a wool fiber dyed so as to differentiate the two parts.

It can clearly be seen that non-DA always faces towards the inside of curvature. The figure shows the existence of a diagonal twist at every transition from the maximum point to the minimum point of the crimps and vice versa.* Non-DA therefore cor-

* Ohara thought that uniform staining occurred at every transition region. As for the twisting in a wool fiber, Rossouw [8] deduced it from his measurements of major and minor axes of the fiber along its length, rotating the fiber by means of a fiber rotator.

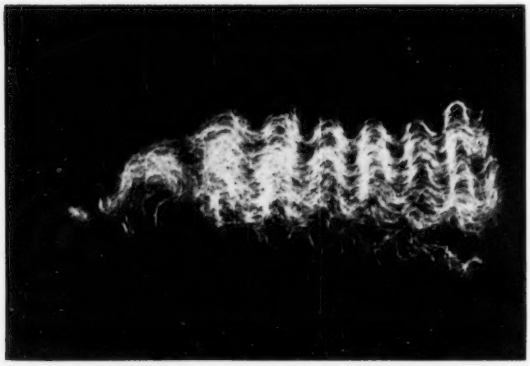


FIG. 4. *Photographic representation of a portion of a staple of wool (magnification, 5×).*

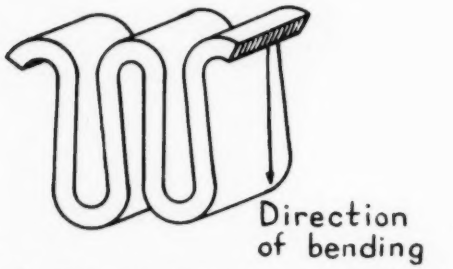


FIG. 5. *Schematic representation of a waved lock.*

responds to part *A* (thick-skinned side), and DA to part *B* (thin-skinned side) of the crimped rayon filaments; Figure 3 corresponds to Figure 11 of the previous paper on crimped rayon filaments. Thus, it should be noted that the bilateral structure of wool fibers, wherever it is crimped, is continuous throughout the entire length from root to tip and is similar in this respect to that of rayon fibers, which are spun through fixed nozzles.

Regular orientation of the cross sections can be shown clearly by the cross section of a tuft of crimped wool fibers. A lock of wool fibers gathering together, forming coincident waves such as shown in Figure 4, was carefully taken out from a population so as not to disturb the original arrangement of fibers as created during the growth, imbedded,* sectioned, and stained by the method mentioned above.

Figure 6 (a and b) shows the section thus obtained, and Figure 5 indicates the sectioned portion of the lock (hatched) schematically. Figure 6 indicates that the cross sections of fibers which form a waved lock are, on the whole, regularly oriented in such a manner that non-DA's face towards the direction of bending. Figure 6 corresponds to Figure 10 of the previous paper which shows the section of a tuft of crimped rayon staple. A schematic representation is given in Figure 15c of the previous paper.

Thus, a close similarity can be seen between the feature of crimping of man-made fibers and wool fibers. The bilateral structure, which can be correlated with the crimps, was detected in the former by an analysis of the shape and skin of cross sections, and in the latter by the differential-staining method. The shape of cross sections and the skin formation of rayon filaments reflect the inner structure of the fibers, as mentioned in the previous paper. The phenome-

FIG. 6a. *Section of a lock of wool fibers (magnification, 180×). The sectioned portion is shown in Figure 5 (hatched). Notice that the cross sections of the fibers in the photograph are facing, on the whole, to the same direction—namely,* non-DA's *face the direction of bending (shown by an arrow). Assume that each fiber has a bending force of unity. Then the vector composition referring to the total number of fibers in the photograph —that is, 42—results in a force of about 36. Hence, 86% of the total force is available in the bending direction. If the disturbance of the arrangement of fibers during the imbedding procedure is taken into account, a greater force than this would have been available in the course of producing crimps on the skin. For the random arrangement of fibers, the approximate resultant force is expected to be as small as* $\sqrt{42}/2 = 4.6$, *and its direction uncertain.*

* See the section on experimental procedure (p. 385).

FIG. 6b. *Regular orientation of cross sections of fibers in a lock of wool.* Non-DA's *face the direction of bending (shown by an arrow).* (*Magnification, 270 ×.*)

non of differential staining of wool fibers also suggest the coexistence of two different inner structures which have different mechanical effects.

Coiling Property of Wool Fibers

According to the theory developed in the previous paper, the crimps of rayon filaments are produced by a resultant force exerted in a bundle of fibers, whilst each individual fiber has only a tendency to coil, rather than to crimp. Experiments show that each individual wool fiber also has only a tendency to coil. Freney [2] made the observation that an isolated single wool fiber coils up in 1% caustic soda. However, no explanation was offered. In order to view the matter in a new light, more material will be presented herein.

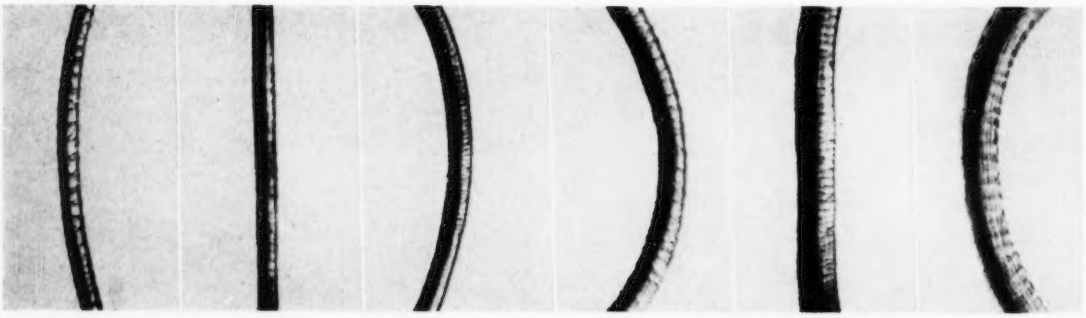
When a wool fiber is straightened by steaming under a small tension and immersed carefully into an appropriate liquid (for instance, in 1% sodium hydroxide solution), leaving both its ends free, it coils up as shown in Figure 7, which is to be compared with Figure 5 of the paper on crimped rayon staple. When the straightened wool fiber is immersed in water, loops are made likewise. In this case non-

FIG. 7. *Coiling of a wool fiber (fine Merino wool) in 1% NaOH. The sample is about ½ in. long and has about three original waves (magnification, 50 ×).*

DA faces regularly towards the inside of the loop, as was the case in the original crimps (see Figures 3 and 10).

If a long wool fiber is anchored at both ends and allowed to lie loosely in 1% caustic soda, as was the case in Freney's experiments, it straightens out at first and then coils up after a certain period of time, but the direction of winding is occasionally reversed here and there along the length of the fiber. To this case also applies the regular orientation of sides. (In 1% caustic soda non-DA faces towards the outside of loops! See the later descriptions and Figure 8c.) It follows, therefore, that the fiber is twisted diagonally at every reversal of winding and the number of right-twining loops is on the whole the same as that of left-twining loops, as long as the anchors are not rotated. The diagonal twist at every reversal of winding can actually be demonstrated by a differentially stained fiber. Freney's loops are to be compared with the S-shaped coiling of rayon filaments, as shown in Figure 6 of the previous paper. Therefore, Freney's effect is the same as the present effect of making single loops.

As discussed in the previous paper, the coiling property of a filament results from its dual construction, which can be compared to that of a bimetallic object. According to the nature of the media surrounding the system composed of two parts, the relative mechanical performance of both the parts in response to the external conditions can change to a great extent. This can produce enhancement or diminution of the coiling property or a reversal of the



a b c d e f

FIG. 8. *Wool fibers in various media at stationary state (magnification, 120 ×). The fibers were differentially stained by Janus Green so as to disclose bilateral structure* (DA *and* non-DA). *The percentages of lateral and axial swelling refer to the original dimensions of each sample in water. The volume swelling was calculated, assuming the cross section to be circular. The fiber samples,* a *to* f, *are not the same, but have approximately the same original fineness.* a—*Water;* non-DA *is situated inside of curvature; swelling: lateral, 0%; axial, 0%; volume, 0%.* b—*0.5% NaOH; straightened; swelling: lateral, + 12%; axial, − 5%; volume, + 19%.* c—*1% NaOH;* non-DA *is situated outside of curvature; swelling: lateral, + 35%; axial, − 16%; volume, + 52%.* d—*3.5% NaOH;* non-DA *is situated outside of curvature; swelling: lateral, + 49%; axial, − 17%; volume, + 83%.* e—*6.5% NaOH; straightened; swelling: lateral, + 61%; axial, − 25%; volume, + 96%.* f—*10% NaOH;* non-DA *is again situated inside of curvature; swelling: lateral, + 69%; axial, − 26%; volume, + 111%.*

fundamental direction of bending.* The degree of coiling is directly proportional to the crimp-forming ability in the sense that the waves produced in a bundle of filaments are finer in a medium where the isolated single filament coils up into a smaller loop, and vice versa. At the critical point where the fundamental direction of bending is reversed, the crimped fiber straightens automatically.

For rayon, the radius of loop made by a single filament became smaller with increasing concentration of caustic soda up to about 4%. When a straight fiber bundle was dipped in this medium, finer waves were produced than in pure water. Further, when fibers already crimped in pure water were dipped in this medium, the pitch of waves was decreased. With increasing strength of alkali beyond this limit, the loop began to be slow-curved. In the medium having a critical strength of caustic soda—usually 6% to 7%—the filament no longer coiled, but remained straight. Conforming to this, the filament bundle did not crimp in this medium, and the fibers which had already crimped were completely straightened automatically in the course of a certain period of time after immersion. In a media having a greater strength of alkali than this critical concentration, the filament coiled up again, but the direction was reversed (see Figure 12 of the previous paper).

An exactly similar effect is observed for wool fibers. Since the latter are more sensitive to alkalies than rayon filaments, the critical concentration of alkali is lower than that for the rayon. Figure 8 (a to f) shows the behavior of wool hairs in media differing in caustic soda content. Wool fibers, stained so as to disclose their dual structure (DA and non-DA), were immersed in (a) water, (b) 0.5% NaOH, (c) 1% NaOH, (d) 3.5% NaOH, (e) 6.5% NaOH, and (f) 10% NaOH. Observations were made at room temperature, and each separate fiber was allowed to lie freely in the respective medium long enough to reach equilibrium.

As shown before, wool fibers as originally grown have crimps in such a regular manner that non-DA faces towards the inside of curvature (see Figures 3 and 8a). In about 0.5% caustic soda the finely crimped fiber is gradually straightened * (Figure 8b). In 1% caustic solution the fiber tends to coil again, but the direction of bending is reversed—namely,

* Reversal of the fundamental direction of bending means the reversal referring to the inner structure—that is, the transition from coiling having non-DA on the inside of curvature to coiling having non-DA on the outside of curvature. This should not be confused with the occasional change in twining direction—for instance, a transition from right-twining to left-twining. In this case, change in direction always accompanies a diagonal twist at every transition point, and the fundamental direction of coiling remains unchanged.

* This critical strength of caustic soda differs to a small extent according to the species of hairs, and for the same species it differs according to the fineness of fibers. The root and tip of the same fiber also may have different critical concentrations.

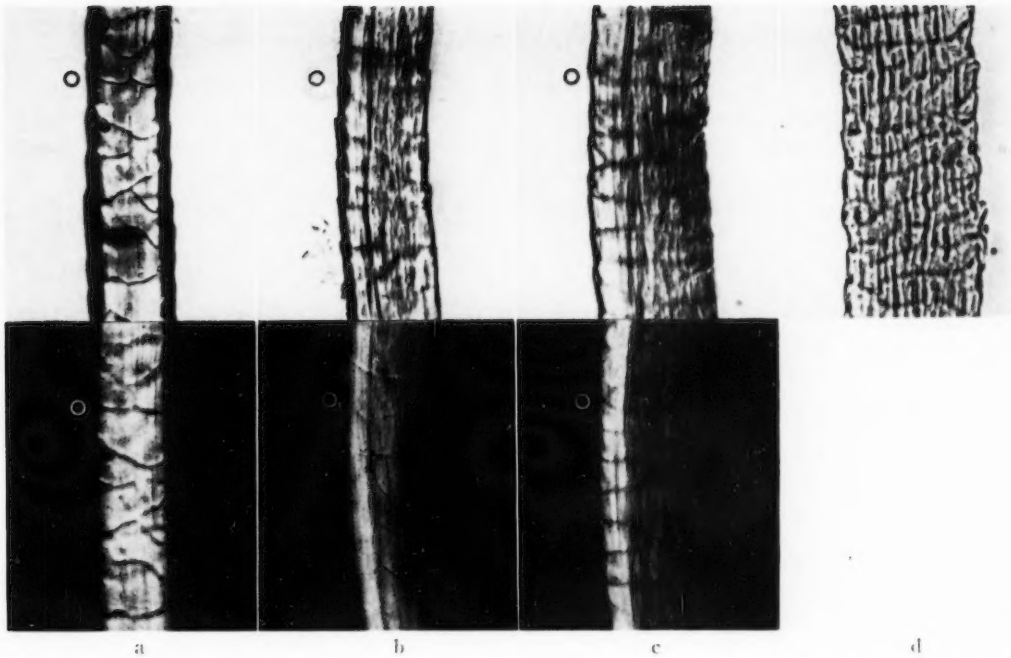


FIG. 9. *Wool fibers in various media observed under the ordinary (upper photos) and polarization microscope (lower photos) (magnification, 400×). The fibers were not stained. The small circles mark the same place in each pair of photographs arranged one above the other.* a—*Water. The fiber is uniformly bright under the polarization microscope with crossed Nicols and the sample in a diagonal position (see lower photo).* b—*1% NaOH. The part which corresponds to* DA *swells and shows the marks of axial cleavage (upper photo). Orientation in this part is disordered and birefringence decays (lower photo).* c—*3.5% NaOH. The part which corresponds to* DA *swells further and is fibrillated (upper photo). Birefringence in this part decays further, but the part corresponding to* non-DA *is as bright as ever, showing its resistance to alkali (lower photo).* d—*6.5% NaOH. No birefringence could be seen under the polarization microscope with crossed Nicols and the fiber in a diagonal position. Both* DA *and* non-DA *are affected drastically.*

the non-DA faces towards the outside of curvature (Figure 8c). With increasing caustic content up to a certain limit, the radius of curvature decreases (Figure 8d), but beyond this limit of concentration (about 5%) the curve straightens again (Figure 8e). In extremely strong caustic solution the bending direction is once more reversed and the non-DA faces the inside of curvature, as was the case in the original fiber (Figure 8f). Thus, there are two reversal points for wool fibers referring to the strength of caustic soda: the first reversal occurs at a caustic soda concentration of about 0.5% and the second reversal at about 5%.

Figure 8 (a to f) represents the state of fibers after reaching equilibrium in each medium. If a dry hair (degreased) is dipped in the 10% caustic soda solution and the state of the hair is watched with respect to the length of time functioning upon it, it represents all the phases, changing from a to f in regular order. Further, when a single hair is first dipped in water for a certain period of time, shifted into 0.5% caustic soda, left there until equilibrium is reached, then shifted into a stronger solution, and so on, in succession, each phase occurs at a stronger concentration than that given in Figure 8. For instance, the state shown in Figure 8f is reached by shifting the fiber into 17.5% caustic soda after passing through the several preceding weaker media in the manner as described above.

The reversal of bending direction as shown in Figure 8 (a to f), can be explained in a manner similar to that for crimped rayon filaments (see the foregoing paper). DA and non-DA have different resistances to alkalies—namely, DA is less resistant to alkalies than non-DA. Non-DA may have been generated having a rubber-like elasticity, while DA may have

developed into a tissue comparable, so to speak, to slightly vulcanized rubber. This would bring about the coiling nature which is characterized by the regular orientation of non-DA on the inside of curvature. When dipped in an alkaline medium, however weak it may be, DA is subjected to a considerable attack, which can be demonstrated by the lateral swelling of this part.* On the other hand, no perceptible change is seen in the structure of non-DA in such a weak alkali.

The action of a weak alkali upon DA may thus be to loosen the cross-linkages between polypeptide chains and allow the chains to coil to increase the entropy, which means, in other words, that the cross-linking elements in DA are very sensitive to alkalies. Thus, DA swells laterally and contracts axially in weak alkaline media. This induces the straightening and reversal of bending.

This action of weak alkali upon DA is demonstrated very distinctly by observations of the fibers under a polarization microscope using crossed Nicols, each fiber specimen being placed in a diagonal position (see the series of photographs in Figure 9). In the normal state DA and non-DA brighten approximately to the same degree and no perceptible difference in birefringence is seen (Figure 9a). However, in a weak alkaline medium, such as 1% caustic soda, where reversal of bending direction occurs, the birefringence of DA decays considerably, while non-DA remains as bright as before (Figure 9b). In 3.5% caustic soda DA is affected so drastically that distinct fibrillation takes place and the birefringence almost disappears (Figure 9c). According to these observations, non-DA, in contrast to DA, is very resistant to alkalies and is not damaged in media containing caustic soda up to about 5%. Alkalies stronger than this limit affect non-DA, and in 6.5% caustic soda the fiber is damaged so entirely that non-DA and DA can no longer be differentiated (Figure 9d). The fiber swells greatly in the lateral direction and contracts in the axial direction, and no perceptible birefringence is observed throughout the fiber.

The conclusion deduced from these experiments is as follows: DA is very sensitive to alkalies, the damage increases with the alkalinity of the medium, but in 5% caustic soda most of the lateral linkages in DA are broken, and the action of stronger alkaline media is directed mainly to non-DA.

Acids react with wool fibers in a different manner. Strong acid, such as 92%–95% sulfuric acid, at room temperature affects non-DA in preference to DA, whereas sulfuric acid having a lower strength attacks DA prior to non-DA.

These experiments demonstrate that wool fibers are substantially bilateral in their structure, and that the coiling property of wool fibers originates from this dual structure.

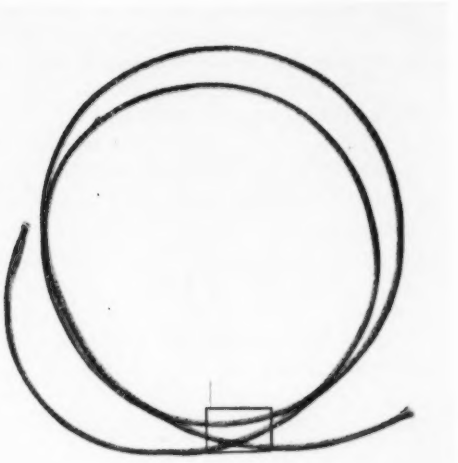
Transformation from Coiling to Crimping

The above discussion dealt principally with the tendency of individual wool fibers to coil. In view of the similarity of the phenomena to the formation of crimp in rayon filaments, it seems of interest to consider specifically the mechanism of crimp formation in wool. Of course, wool hairs and rayon filaments differ in their origins, in modes of production, and in composition. It is possible that other properties of wool hairs than those treated in this paper as well as biological and histological conditions during hair growth play an important part in crimp production, but the important point is that both kinds of fibers have the dynamic principle in common. Based upon the phenomena as presented before, an analogous interpretation will be given below. Needless to say, this should be furnished with more biological information.

The dynamic principle which was offered in the previous paper concerns the fact that crimps are produced in a bundle composed of a huge number of fibers having a pronounced tendency to coil. If individual fibers are separated, they tend to coil, each fiber in its proper direction. However, when the fibers are tightly packed and restricted from free movement, the actual force available in the system is a vector sum of individual coiling forces. A dynamic analysis of this system indicates that the individual fibers are apt to be subjected to a torsional effect.* This effect propagates itself all over the system, and eventually all of the fibers tend to the same direction, conforming to that of the inducing force, as shown in Figure 6. In consequence, the bending force of the system is greatly increased, and this lock of fibers bends in a body to the same direction. This perform-

* Neutral water also has influence upon DA. The change caused by neutral water and by a very dilute alkali is reversible—that is, the fibers regain the crimps after drying. This is important in connection with the practice of laundering and felting of wool fabrics.

* Such a great difference between torsional rigidity and bending modulus as in the case of rayon filaments cannot be observed for wool hairs [7]. Even in this case, however, the analysis shows that the torsion can happen in preference to the change in bending curvature.



a (60 ×)

b (550 ×)

FIG. 10. *Loops made by a wool fiber under steaming* (a). *The fiber was differentially stained by Janus Green. Notice that* non-DA *faces towards the inside of loops. The portion in the box in the upper photograph* (a) *is magnified in the lower photograph* (b).

ance of fiber mass induces the counter-action towards the roots of individual fibers, as can be seen at the supporting point of a cantilever.* This results in bending in the opposite direction of the part growing subsequently. The repetition of these effects results in crimp formation. An explanation of the peculiar behavior of twist in a wool fiber as described by Rossouw can be given by these considerations—namely, the fiber should be twisted diagonally at

* It is not necessary to compare the supporting point of cantilever to a follicle. The counter-action can rather happen above the skin.

a

b

FIG. 11. *Straightened bundle of wool fibers in air* (a). *When immersed in 1% NaOH, the bundle produced crimps* (b).

transitions between crests and troughs of waves. Furthermore, it is rather natural to expect from this interpretation that the direction of twisting should be reversed alternatively. More detailed dynamic considerations are given in the previous paper.*

The coiling and crimping nature of wool hairs could be demonstrated by several other experiments. A degreased wool hair was straightened in 0.5% caustic soda under a slight tension, washed with water, and dried. On steaming in a relaxed state, the fiber coiled spontaneously, as shown in Figure 10a. It can be seen in this figure that non-DA is located on the inside of the loops. This is shown more clearly in Figure 10b, which shows part of Figure 10a in a greater magnification. When the fiber was dipped, instead of steaming, in 1% caustic soda, loops were made likewise (Figure 7), but non-DA faced towards the outside of curvature (see Figure 8c).

A bundle of wool hairs (more than a hundred fibers) was stretched, dipped in 0.5% caustic soda, washed with water, and dried under tension as before. Both ends of the bundle were tied by fine strings so as to prevent the separation of individual fibers (see Figure 11a). The bundle was then im-

* In this connection, it is of interest that Woods [11] thought out the analysis of fiber forms, differentiating the crimp of fibers in a staple from that of single fibers withdrawn from a staple. According to Woods, wool fibers in the staple are generally set in a state of strain, and if keratinization could occur while the fiber were free from external force, the fiber would assume a different form—that is, the "structural form" determined only by the conditions of growth.

mersed in 1% caustic soda; instead of coil formation, wave formation occurred, as shown in Figure 11b. If single filaments had been separated before immersion, they would have coiled as shown in Figure 7, or formed a spiral as shown by Freney.

Thus, similar phenomena to those for rayon filaments apply to wool hairs also. In the case of wool, however, it is difficult to duplicate the wool staple as it grows on the skin, and therefore such crimps as originally occurred could not be reproduced. Nevertheless, the experiments served to demonstrate the principle underlying this theory of crimping.

Wool fibers grow closely together and stick to each other during the growth by the action of grease, sweat, scaly surface, and so forth, and form themselves into clusters composed of adhered hairs all over the skin. Therefore, individual fibers cannot act independently, and are in this respect similar to the state of pressed rayon filament bundles.

The conspicuous feature of crimps of wool hairs and rayon filaments consists in the fact that a great number of fibers composing a lock perform in a body and form coincident waves, as can be seen in Figures 1a and 4. A satisfactory explanation of this can be given by the present mechanism of crimp formation.

According to the histological study of Wildman [10], the wool follicle, before the fiber pierces the skin, takes the form of a short spiral, and always has two spiral loops in the longitudinal direction, irrespective of its depth in the dermis. Accordingly, the deeper the follicle lies in the dermis, the greater the pitch of the spiral in the longitudinal direction and the smaller the amplitude in the transversal direction. Immediately above the skin the fiber is seen to be in the form of spiral (coiling) possessing the same pitch as that of the follicle beneath the skin. Furthermore, it can be expected from Wildman's observations that the depths and dimensions of follicles, even those of follicles lying directly contiguous to each other, differ multifariously. Therefore, the individual fibers which form themselves into a coincidentally waved lock must have come out of follicles differing in character.

The statement of Wildman suggests that each single fiber forms a spiral, and his information about the state of fibers immediately above the skin reminds one of the similar state of rayon filaments at one end of a crimped bundle, where each single fiber forms a coil in proper manner according to its coiling ability and coiling direction, as shown in Figures 13 and 14 of the previous paper. It is also quite the same that coiling is at once transformed into a regular waving towards another end accompanying a diagonal twisting at every transition from a maximum point to a minimum point of waves.

As can be seen in Figure 6, the fibers composing a lock which has a coincident waving have different cross sections varying in diameter and in shape.* This difference would be due to the characteristic natures of individual follicles, and suggests that individual fibers have different coiling natures, as can be demonstrated. That the fibers nevertheless make the same waving can be explained satisfactorily by the present interpretation for crimp production. In this case also, the pitch of waves of the lock is conditioned by the average coiling property of individual fibers, as was the case in tufts of rayon staple.† It is pertinent to assume that no proper inborn waving ‡ belongs to each single hair.§

According to the experiments, it seems to stand to reason that finer fibers have, in a statistical sense, greater coiling ability. Therefore, the clusters at a certain area on the skin where the hairs are finer on the average have finer waves than the clusters composed of statistically coarser hairs.‖

Another complexity of wool hairs consists in the fact that the diameter and coiling ability of a single fiber differ along its length. However, the rule in the previous paper was found to be applicable in this case also—namely, the waves of the fiber portion which is located in a plate-like cluster are uni-

* Rossouw also noticed that the fibers which are involved in an even and regularly waved lock and have the same number of crimps per unit length have different fineness. They belong, according to him, to quality classes ranging from 56's to over 90's.

† See the variety of diameters of coils in Figure 5 of the previous paper.

‡ Should be differentiated from "coiling" or "spiral formation," which is characteristic of each single fiber.

§ Further demonstrations can be made to show that the same relationship exists for human hair. Every single hair of people who have wavy hair is beautifully coiled. When tonic or oil is applied and the hair is combed, they behave in a body and produce waves, while individual hairs are twisted diagonally at every transition from crest to trough of waves. Permanent-wave setting of women's hair by electric heating is also based on the same principle. This process, which perhaps resulted from experience, does not set the waves, but imposes a thermal setting of coils. After being oiled and combed, however, the hairs produce waves. The significant point is that diagonal twisting is produced at every transition from crest to trough of waves.

‖ The relationship between the number of crimps per unit length and cross-sectional area of individual hairs, as presented by Barker [1], is true only in a statistical sense, as mentioned here.

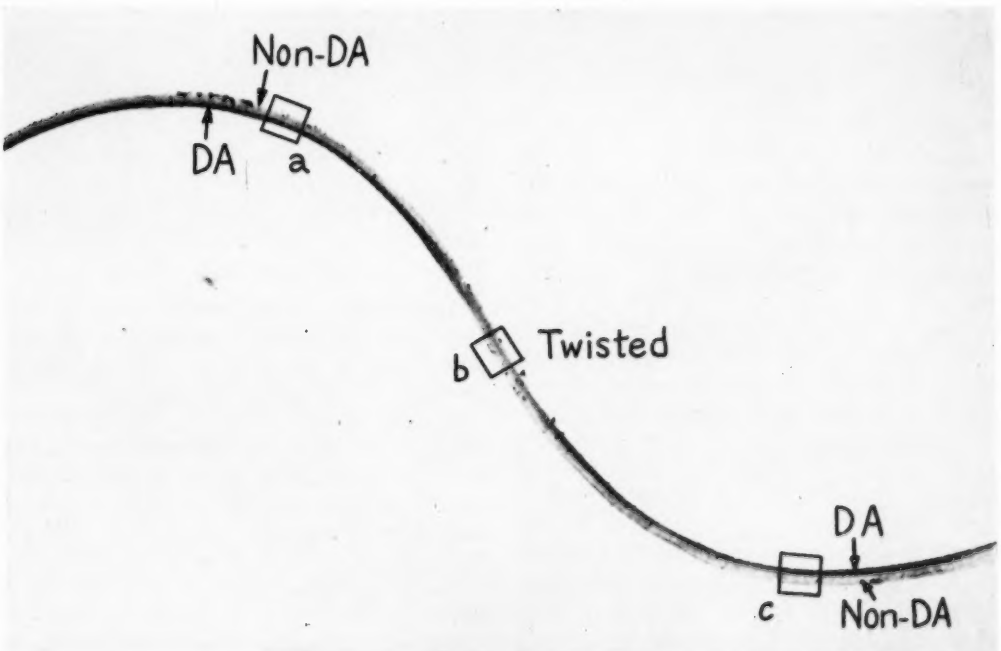
planar, while the waves are three-dimensional in the portion where the fiber is a member of a rod-like cluster (refer to Figures 17 and 18 of the previous paper). Thus, transitions from uniplanar to three-dimensional waves occur often within a single fiber.*

Discussion on Bilateral Structure

Attention has been directed in this paper to the bilateral structure of wool fibers, which was demonstrated by differential staining and resistance to chemicals. Partial staining itself in general is not new, and has been seen frequently in research and in practice. The important point concerning the differential staining as developed in this research consists in the connection of this with the coiling and crimping of wool fibers and in the idea that crimp formation is due to the intrinsic nature of the wool fibers to coil.

Light and weathering during the growth might indeed cause the heterogeneity of hairs, which might be differentiated by some means or other, but it is hardly assumed that such accidental changes in structure should so regularly be correlated with the coil-

* See in Figure 4 that the tip of the plate-like lock is, so to speak, rod-like shaped. Rotation of wave plane from root to tip also is quite possible. (Refer to Rossouw's observation.)



(Magnification, 100 ×)

a *(800 ×)* b *(800 ×)* c *(800 ×)*

FIG. 12. *Part of a wool fiber stained differentially by Ponceau 2R.* Non-DA *faces towards the outside of curvature, and the relationship is contrary to that of Figure 3.*

ing and crimping nature of wool hairs as treated in this paper.

According to the method used in this research, differential staining happens in the same manner irrespective of the state of specimens—namely, for the staining of both the sections and entire fibers. Therefore, a greater or smaller permeability of cuticle on any one side of the fiber has no bearing on the partial staining. Furthermore, as can be seen in Figure 2, the demarcation line between DA and non-DA seems to be too sharp to be attributed to the difference in permeability.

The fact that DA and non-DA have different resistance to chemicals—namely, DA is resistant to strong acid, while non-DA is resistant to alkalies—suggests that the difference between them is substantial. A similar difference occurs in staining. When some basic dyes are used, as is the case in this research, the inside of curvature is less accessible to the dyes (non-DA) and the outside of curvature is more accessible to the dyes (DA). One thing worth noticing is the reversal of DA and non-DA which happens when an appropriate acid dye, such as Orange G, is used, as discovered by Ohara. Further experiments showed that Ponceau 2R * is more useful for demonstrating the reversed differential staining.† Figure 12 shows part of a wool fiber stained by Ponceau 2R. It can be seen that the inside of curvature is stained in a deeper tone than the outside, and the relationship is contrary to that shown in Figure 3. This indicates that the inside of curvature is more basic and the outside is more acidic.‡ A diagonal twist between the maximum and minimum points of waves can clearly be seen.

All these phenomena seem to endorse the opinion that the bilateral structure which has been treated in this paper is an intrinsic characteristic of wool fibers. In this respect, it is, on the one hand, important to develop the problem by referring to the biology of hair growth. On the other hand, this seems to be significant for physical and chemical studies on wool fibers. The keratin molecule is a complex polypeptide constituted of a number of diverse α-amino acids which not only are united by condensation into polypeptide chains, but also are characterized by a variety of types of cross-linkages. The physical properties of built-up materials are influenced by the kinds of amino acids combined together. Thus far, analyses have been made in reference to the hydrolysis of whole wool fibers, and no attention has been paid to the distribution of amino acids in a fiber. According to the present work, a hair can be divided along its length into two parts which differ markedly in dyeing and in chemical and physical properties, and it is this duality which produces crimp, which is the most important characteristic of wool. It stands to reason that the chemical constituents of these two parts should be different. The elasticity and over-all stress-strain curves of wool fibers have been successfully explained by taking into account the crystallographical character of the keratin molecule, such as the intramolecular transformation from α- to β-keratin and the reverse process, and by the analysis of the behavior of various types of cross-linkages. For the completion of these interpretations, the microscopic character of wool as revealed here will be of importance. On that account, the physical and chemical analyses of the dual structure of wool fibers constitute a new approach in wool studies.

Composition of Waves

According to the explanation of crimp formation as developed in this paper as well as in the previous paper, it can be assumed that each wool hair is not endowed with a definite shape of crimps, but only with the ability to coil. The dynamic effects produced in a system composed of a large number of fibers, each fiber having coiling action and other mechanical properties, decide the shape of crimps and the number of crimps per unit length. To show the incidental nature of the shape of wool crimps, some illustrations concerning the composition of waves will be given.

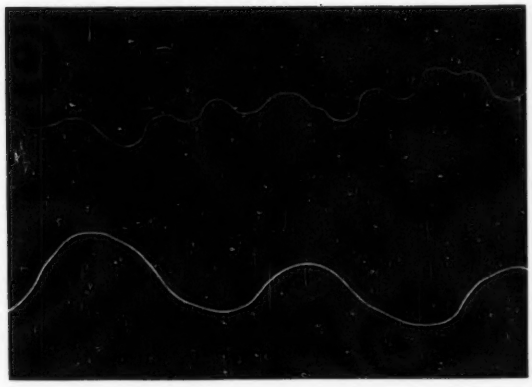
Two wool fibers having waves differing in shape and pitch, as shown in Figure 13a, are greased and united by drawing them several times between thumb and forefinger from the one end to the other and relaxed. Then a new type of wave, as shown in Figure 13b, is produced. The waves thus produced cannot always be predicted from simple superposition of wave trains, since the fibers are apt to be twisted.

Next, two wool fibers having waves with almost identical pitches and amplitudes are fixed at one end in such a manner that the phase lag is just half wave length (see Figure 14a), and are greased and drawn as before so as to unite the fibers. When the fibers are relaxed, very regular waves are produced, whose

* Sodium salt of *m*-xylene-azo-β-naphthol-3 : 6-disulfonic acid (Rowe's Colour Index, No. 79).

† Experimental procedure is described in a later section (p. 385).

‡ This accounts for the fact that the outside of curvature of wool hairs is strikingly sensitive to alkalies.



a

b

FIG. 13. a—*Two wool fibers having different waves.* b—*Two fibers united by grease.*

amplitude and pitch are almost the same as those of the individual fibers (see Figure 14 b). In this case, also, there is no compensation of waves due to interference occasioned by the phase lag, since the fibers can be twisted.

These illustrations support the interpretation that the crimps are not a fixed property of individual fibers. When two fibers united together as shown in Figure 13b are kept in that state for a long period of time, the new type of crimp is set and the individual fibers no longer regain their original shapes even after they are separated from each other by extracting the grease. Notwithstanding this fact, the coiling ability which results from the inherent nature of individual fibers will not be changed at all.

Experimental Procedure

Differential Staining by Janus Green

Entire fibers.—The wool fibers are degreased by the alcohol-benzene or alcohol-ether mixture (1 : 1 by volume) using a Soxhlet apparatus. The degreased hairs are dipped in 0.1% water solution of Janus

a

b

FIG. 14. a—*Two wool fibers having similar waves.* b—*Two fibers united by grease.*

Green. Distilled water is used to dissolve the dye and no other agent is added. The mixture is warmed on a water bath up to 60°C for 1–2 hrs. Even in this stage, two parts differing in color density can be differentiated for each fiber by examination under a microscope. The hairs are dipped in 1% acetic acid or 0.5% hydrochloric acid or sulfuric acid at room temperature for about 5 min. and washed with water; then the difference in color density becomes more apparent. The direction of crimping does not change throughout the whole procedure.

Sections.—The degreased fibers are imbedded by the agar-agar paraffin method [4] and sectioned. The sections fixed on a slide are subjected to the same staining procedure as before.

Differential Staining by Ponceau 2R

The fibers are degreased as before and dipped in 0.1% dye solution. The mixture is warmed to 60°C and kept for about 30 min. at this temperature, and the fibers are taken out and washed. In this case the pH of the dye solution is very important and must be adjusted to 7.0 by dissolving the dye in the appropriate buffer solution. When the pH of the solution is lower than 6.0 or greater than 8.0, the fibers are uniformly stained and no differential staining occurs.

Imbedding of Wool Lock

A portion of a wool lock composed of fibers packing together forming coincident waves is carefully taken out from a population so as not to disturb the original regular arrangement of fibers and is dried in an oven. This portion of lock is immersed slowly in a monomer liquid of butyl methacrylate containing a small amount of benzoyl peroxide as polymerizing catalyst. The mixture is warmed to 40°C and kept for about 8 hrs. at this temperature until it solidifies to a block having an appropriate hardness for sectioning.

The collodion also can be used as an imbedding material. In this case, however, the original arrangement of fibers in the lock is apt to be disturbed, since the imbedding process involves several stages of operation.

Agar-agar method or others which use water media cannot be used, because the crimped fibers have a marked tendency to be extended in water and the fibers in the lock are considerably disordered.

Summary

1. Differential staining of wool fibers under controlled conditions by using several basic dyes can reveal the bilateral structure. Janus Green has proved to be the best dye for this purpose. The part stained in the darker tone is dye-accessible (DA), and the lighter part is less accessible to the dyes (non-DA). The differential staining as described in this paper can be correlated with the coiling and crimping of wool fibers.

2. Isolated single fibers of wool show a pronounced tendency to coil rather than to crimp. In the air or in neutral water non-DA always faces towards the inside of curvature. This coiling is a result of the bilateral structure of wool hairs, which can be compared to that of a bimetallic object. Thus, the fiber behaves differently according to the external conditions, and in alkaline media a reversal of coiling direction occurs.

3. The analysis of waves of wool fibers shows that non-DA is regularly situated in the inside of curvature, with a diagonal twist at every transition from crest to trough. The bilateral structure runs continuously throughout the entire length of fiber from root to tip.

4. The mechanism of crimp formation is discussed. When a large number of fibers are packed together, each individual fiber cannot coil in its own way and the resultant force available in the group produces crimps. The mass of fibers having, on the whole, greater coiling action produces finer waves and vice versa. The shape of the wave is thus determined by the nature of the mass. It seems pertinent to assume that the intrinsic nature of wool fibers is the coiling due to the bilateral structure, while waving or crimping results from the action effected in a mass of fibers having coiling nature. Evidence is given to support this opinion. The peculiar behavior of the twist in a wool fiber also can be explained by this mechanism of crimp production. It is pointed out that the phenomena treated in this paper are quite similar to those which were observed for crimped rayon staples.

5. The staining behavior is reversed when buffered solutions of appropriate acid dyes, such as Orange G and Ponceau 2R, are used. In this case the inside of curvature is stained a deeper tone than the outside, and the relationship is opposite to that in the case of basic dyes. This suggests that the inside of curvature is more basic and the outside is more acidic. In conformity with this, the outside of curvature is very sensitive even to very weak alkalies.

6. The incident nature of the shape of waves is demonstrated by experiments on wave composition.

Acknowledgment

The authors wish to express their sincere gratitude to the late Professor Emeritus G. Kita for the constant interest and encouragement given to this work. They also express their indebtedness to Mr. K. Sekimoto for assisting with the experiments. They are further indebted to the Grants for Scientific Research of the Government, Research Institute for Synthetic Fibers, Japan (Nippon Kagaku Sen-i Kenkyusho), and Japan Synthetic Textile Association for financial support.

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(*Manuscript received October 7, 1952.*)

Comment on the paper, "Crimping of Wool Fibers," by M. Horio and T. Kondo

The Editor has given me the opportunity of reading the above paper by Horio and Kondo before publication and of adding the following comments.

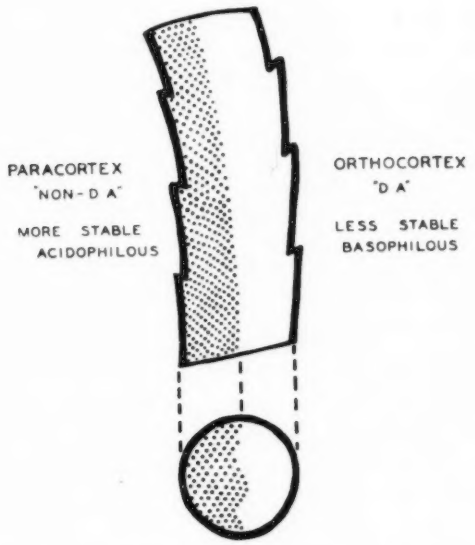

FIG. 1. *Nomenclature and properties of the unsymmetrical cortex of the wool fiber.*

My studies on the stability and digestibility by enzymes of the two parts of the cortex of wool fibers * are a confirmation of the unsymmetrical structure deduced by Horio and Kondo from dyeing studies. In view of the possible importance of this structural peculiarity of wool, it is gratifying to have available the two approaches.

The question of nomenclature is important, if only to avoid clumsiness in discussion. Horio and Kondo designate the two parts of the cortex as "dye-accessible (DA)" and "non-dye-accessible (non-DA)"; I have used the terms "paracortex" and "orthocortex." The accompanying sketch may assist in associating properties and names.

There is a minor difference in our points of view concerning the differences between para- and orthocortex. Horio and Kondo seem to imply that the paracortex (non-DA) is more rubbery, and that the orthocortex (DA) is more vulcanized. Their reasons are not clear, since their relevant experiments are similar to my own, which imply the lower stability in the orthocortex—*i.e.*, less "vulcanization" or keratinization.

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The Heterogeneity of the Keratin Fibers

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HAIR AND WOOL are very resistant chemically, and this property is usually ascribed to their consisting largely of keratin, a protein stabilized by an extensive cross-linking of polypeptide chains by disulfide bridges. These fibers are not, however, entirely uniform in composition; they exhibit, in fact, a well-defined histology pointing to variations in the nature of the keratin and to the existence of several different constituents, some of which, although comprising only a minor fraction, seem to be more resistant chemically than the bulk of the fiber. The existence and inert character of these constituents are revealed by experiments in which the keratinous fraction of the hair is dissolved or destroyed, leaving a residue of more stable components. In recent years some attention has been paid to these minor constituents, with the object of determining their histology, their chemical constitution, and their contribution to the properties of the whole fiber, since this may be of some practical importance.

For the purpose of this article, the term "keratin" will mean, as in the sense used above, a protein of the α-type—*i.e.*, yielding a large-angle α-type x-ray pattern—stabilized by the cross-linkages formed by the disulfide bridges of cystine residues. More precise definitions in terms of amino acid ratios have been advanced, but are of no advantage here. The nonkeratinous proteins are the other proteins of the hair, some of which may be more insoluble than the keratin. Such components may consist of a protein structurally similar to keratin in combination with a carbohydrate or lipoid, but little is known of their composition or of the reasons for their stability, and it is important to elucidate these questions.

Hair is divided into cuticle, cortex, and medulla; in each of these regions resistant, nonkeratinous constituents are found. Much of the discussion of resistant constituents has concerned their location within these regions. The main object of the present article is to consider some of these problems and to point out where further clarification is necessary. Each of the three divisions will be dealt with in turn.

The Cuticle

General agreement has been reached concerning the histology of the cuticle. The keratinous fraction itself is not uniform in properties, and may be divided into two parts on the basis of relative resistance to digestion by proteolytic enzymes. The more resistant part forms a sort of denser shield or skeleton of the cuticular cells. It is cast into furrows and fissures, which, extending parallel to the fiber axis, may give rise to a rippled external surface often noted in replicas of the surface. Imbedded in the furrows is a less resistant fraction which is etched away by the enzymic treatment. Probably these two fractions differ only in their degree of hardening—*i.e.*, of cross-linking by cystine bridges. Zahn [32] referred to these parallel ridges as "fibrils," but the electron-microscopical observations of the present author do not support the view that they have a fibrous texture.

The most resistant fraction of the cuticle is a thin external membrane, named from its position the "epicuticle." Since it completely ensheathes the scales externally, the epicuticle may remain as a continuous tubule, thickened by much adhering material derived from the cuticle cells, when the fiber is partly dissolved. Such tubes may be referred to as "cuticular sheaths" rather than "epicuticle" since they are not a single component (Figure 1). This membrane is very thin (100–200 Å.), and it has been assumed in many publications that it can only be seen in the electron microscope and that it was

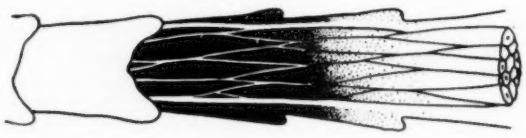

FIG. 1. *Sketch to illustrate the histology of the various resistant membranes resulting from the solution of the keratin (shown in black) of hair.*

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discovered only as a result of the development of this instrument. The limitations imposed by the resolving power of the light microscope apply only to the study of cross sections, in which the epicuticle is placed end-on and is in this direction too thin to be resolved. Separated from the fiber as an extensive sheet, it may readily be seen by means of the light microscope when it is stained, or when separating two liquids differing in refractive index (*e.g.*, in the Allwörden reaction), or by reflected light, or by phase contrast.

The first mention of a thin resistant external membrane was made in 1886 by McMurtrie, who noted that the external layers of the cuticle resisted the destructive action of caustic soda, and supposed that this might be due to a thin membrane. His drawing and description are accurate and complete. He wrote [20]:

"Nor have we been able to determine the manner in which the scales are joined to each other. There are many reasons to support the conclusion that they are attached to a special membrane surrounding the fibro-cellular cylinder, a membrane exceedingly thin and transparent, and difficult to detect even under the most favored condition. This layer or membrane with its scales, like the contents of the pigment canal, seems much less soluble in strong alkaline solutions than the fibro-cellular mass, and while the latter is rather quickly broken down and dissolved by the reagent mentioned, this with its scales remains intact for a long time under the same treatment. This becomes apparent if a fiber of the coarser wools be placed upon a glass slide and covered with a small quantity of a strong solution of potassium hydroxide (caustic potash) and left for some time to digest. The same effects may be obtained more readily by careful heating.

"By observing the fiber, from time to time, and gently crushing it by pressure upon the cover glass, the fiber will be seen first to swell and show the characteristic markings due to the scales, then to exhibit the outlines of the elongated cells of the inner cylinder, and very soon the latter disappear completely by solution, leaving the membrane in question in patches over the plate. We have succeeded admirably in separating the scales by this method, as may be seen from the reproduction of the photograph we have to present herewith, Plate XI, showing that in the case of Cotswold wool, either the scales are attached to an exceedingly thin membrane or they are joined to each other by their edges."

Various authors, and in particular Müller [26], realized that the bubbles which appeared on hairs when immersed in chlorine water were enclosed in an exceedingly thin membrane. Lindberg [18] demonstrated its existence beyond question by means of electron microscopy, and this instrument remains the most convenient for its investigation. Recently Ames [2] has managed to detect it in cross sections in this way.

This membrane seems to be the most resistant fraction of the whole fiber, and remains almost invariably when the bulk of the fiber is destroyed. The present author, working with various colleagues [21, 24], has established its presence by means of the light microscope and the electron microscope in the residues remaining after the following treatments: (*a*) tryptic digestion; (*b*) peptic digestion of reduced fiber; (*c*) solution by means of strong urea solution containing reducing agents; (*d*) solution of oxidized fibers in dilute ammonia; (*e*) solution of reduced fibers in dilute ammonia; (*f*) digestion of supercontracted fibers by enzymes; (*g*) solution by 30% formalin at 130°C; (*h*) accelerated digestions [17]; and (*i*) digestion by insects [5, 19].

The membrane is also relatively resistant to acids —*e.g.*, carbonization in sulfuric acid has little effect— but is hydrolyzed by prolonged boiling in acid solutions to yield a mixture of amino acids [15, 29, 32] and probably carbohydrates [15]. The torn fragments released by bursting the bubbles produced by the action of chlorine on fibers are altered during this treatment since they can now be digested by trypsin—further proof of a protein base.

Zahn, following Müller, questioned whether the epicuticle is an entirely external membrane or a cell membrane enclosing individually each flattened cuticle cell. Müller favored the latter view, deriving his opinion from a study of the Allwörden bubble formation, but the formation of the bubbles and their growth from single bubbles covering one scale to giant formations covering several scales is not easily reconciled with the view that each individual scale is enclosed in a separate membrane [25]. Other evidence suggesting that the epicuticle is an entirely external membrane is (*a*) the isolation of sheets of epicuticle large enough to cover several scale faces, (*b*) the separation of continuous tubules consisting of the surface layers of the cuticle when the cortex,

etc., are dissolved (see next section), (*c*) the lifting off of a continuous membrane when a fiber exhibiting a "normal" chlorine-induced bubble reaction is transferred to an alkaline medium, (*d*) the separation of a continuous sheath when supercontracted fibers are digested for several days in trypsin, (*e*) the epicuticle-like sheath on whale hair, which lacks a normal cuticle, and (*f*) the sheath extending beyond the point at which a normal bubble reaction on individual scales can be elicited in the growing hair in the follicle.

It has been demonstrated in sections [29] and in plucked hair roots that this membrane is present on the growing hair deep within the follicle at a level at which the hair is just beginning to harden [10, 23]. It seems probable, then, that the epicuticle has a role in the complex events of hair growth.

The Cortex

Much discussion has centered around certain resistant constituents which, as will be shown below, are found in the cortex of the keratin fibers. Difficulties were experienced in determining the nature of these constituents, chiefly because the methods of preparing resistant fractions usually involved the partial solution of the fiber, with the consequence that few points of reference remained to assist in locating the residues. Most procedures which remove the keratin proper leave a confusing mixture of resistant fragments derived from all three histological regions. The situation was not improved by the introduction of names having histological implications before the histology was fully determined.

Several authors—Lehmann [16], Elöd and Zahn [7, 32], and Alexander and Earland [1]—have described procedures which claim to yield preparations of a resistant sheath, membrane, or pellicle underlying the cuticle (subcutis or subcuticle), or lying between the cortex and the cuticle (Zwischenmembran), or composing an external mantle to the cortex (cortical mantle). Mercer, Lindberg, and Philip [21] examined several such preparations and showed that the tubular forms came from the external layers of the cuticle. The present author added a further demonstration by partially coating the outside of the fiber with metal, and isolating the sheaths bearing the metallic "label" [22].

In most preparations, however, in addition to the tubular cuticular sheath, which is clearly visible in the preparations shown in Figures 2 and 3, cortical residues were present, including some cortical cells, more or less intact, which had escaped solution [6, 11, 24]. The existence of these residues, which is particularly well demonstrated by the method of Alexander and Earland and by Zahn's procedure of warming fibers in strong caustic potash solution, led these authors to assert that they had discovered a membranous tube definitely lying beneath the cuticle.

Observations on Cross Sections

In order to determine more definitely the nature and location of these residues, it was decided to carry out the experiments using cross sections of hairs instead of complete fibers, and to follow the course of the reaction microscopically.

Method of Alexander and Earland [1].—Small locks of human hair, merino wool, and whale hair were immersed in 1% aqueous peracetic acid for 24 hrs., removed, washed free from acid, and dried.

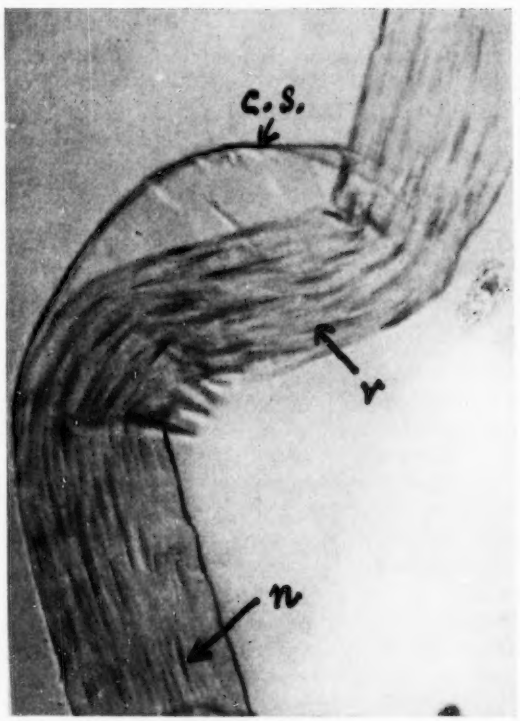


FIG. 2. *A wool fiber oxidized with peracetic acid and treated with sodium bicarbonate solution. The cuticular sheath* (c. s.) *and the cortical residue (cell membranes)* (r) *are visible. Within the cortical residue the nuclear remnants* (n) *appear as elongated objects. Compare with cross-sectional views in Figure 4. (Optical micrograph; unstained preparation.)*

The peracetic acid ruptures the disulfide cross-linkages of the keratin, and the altered protein is soluble in alkaline media. Cross sections of the oxidized hair (and wool) were then cut using the Hardy microtome, and mounted in water on a microscope slide. It was usually possible to find a field in which both cross sections seen end-on and short lengths seen from the side were present, enabling the action to be viewed simultaneously from the two directions. Dilute ammonia (0.1*N*), and in some experiments 1% sodium bicarbonate solution (pH 8.3), was then allowed to run under the cover slip and displace the water. An immediate swelling of the sections occurred, causing the fiber to increase to about three times in diameter. Photographs of swollen cross sections are given in Figure 4 (a, b, and c). It will be seen that the structures which do not dissolve are: (*a*) the external layer of the cuticle (cuticular sheath) (This conclusion also followed from an examination of the sections lying side-on, and was previously demonstrated by Mercer and Golden [25] using whole fibers.); (*b*) the cell membranes of the cortical cells; and (*c*) various minor components appearing as particles or rodlets within the cortical cells. (See Figure 1.)

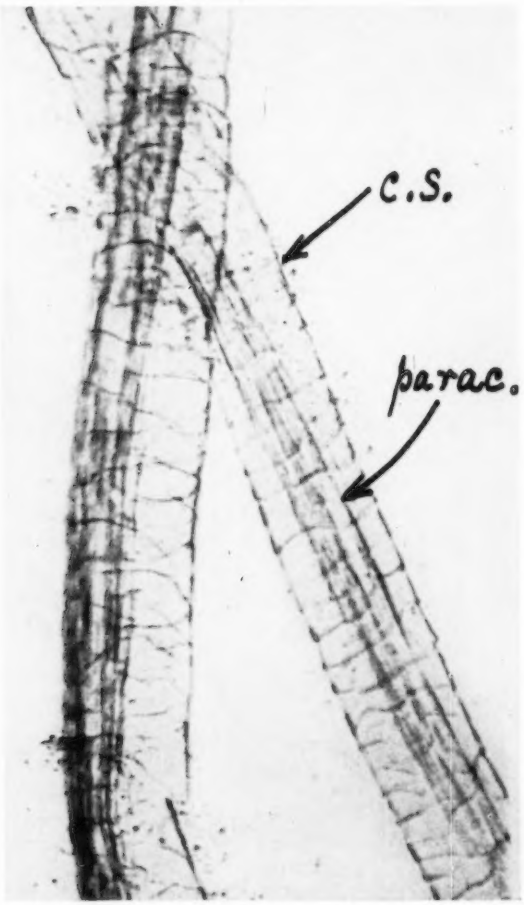


FIG. 3. *Longitudinal view of unsymmetrically supercontracted wool fibers after 24 hrs. digestion. The cuticular sheath* (c. s.) *may be seen enveloping the resistant fraction of the cortex (paracortex)* (parac.). *(Treatment: fibers heated in water at 120°C for 1½ hrs., and digested 24 hrs. with trypsin. Optical micrograph; unstained preparation.)*

Heating in Caustic Potash Solutions (Zahn's Method).—Wool and hair (unoxidized in this case) were cross-sectioned and mounted as before, and treated with 2*N* caustic potash solution. The mount was warmed gently near 100°C over a small flame, and examined microscopically at intervals. The sequence of events was much as described above—*viz.*, swelling and partial solution, leaving a residue of cuticular sheaths and cortical cell membranes.

In both experiments the appearance of the sections seen from the side (longitudinal view) was as described by Zahn and Haselmann [33, 34] and by Alexander and Earland [1], and as illustrated in their photomicrographs. The difficulty in recognizing the true nature of the cortical residue when viewed from the side may be appreciated from a study of Figure 2.

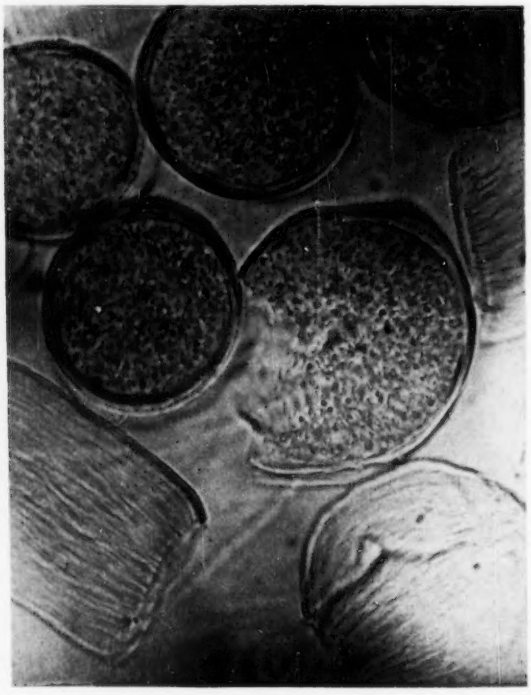
These experiments prove that the subcuticular resistant constituents do not form a coherent skin or pellicle lying immediately beneath the cuticle, but are, on the contrary, true cell envelopes distributed throughout the cortex. Second, they demonstrate the important fact that the cortical cell membranes are composed of a substance which owes its chemical resistance to some chemical factor other than disulfide cross-linking since these cross-links should be destroyed by oxidation.

These findings have the interesting implication that the fibrous keratin itself, which constitutes about 90% of the fiber, is present in the form of small "packets," each wrapped in the resistant nonkeratinous cell membrane, as has been suggested in Figure 1. It is very likely that such a structure would have some influence on the movement of mobile molecules through the fiber and should therefore be of some importance in technological processes. The cortical cell membranes, plus the resistant fraction of the cuticle, constitute between 7% and 10% [1]

of the total weight of the fiber, and this fraction cannot be altogether negligible in its effect on certain physical properties of the fiber.

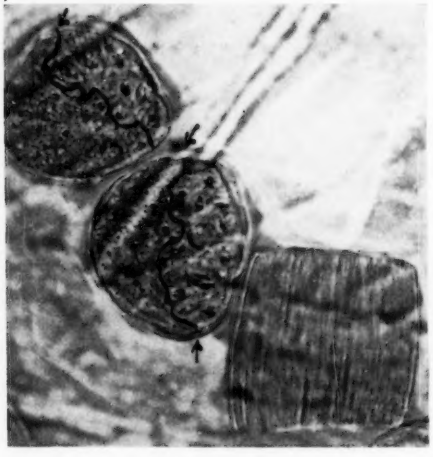
Since epicuticle and cortical cell membranes may occur mixed together in some preparations, it is probable that the two have been confused, since they can scarcely be distinguished in the light microscope. When electron micrographs are compared, however, some distinguishing features may be noted. Fragments of epicuticle usually are uniformly thin unwrinkled sheets, with a few characteristic folds and curls which seem to be produced when the membrane is dried on a substrate for examination (Figure 5a). In contrast, the cortical cell membranes exhibit many fine approximately parallel "pleats" or "gathers," which seem to be original features arising from the fact that the closely packed cells meet in interpenetrating surfaces having a fine irregular plication, which may be seen in cross sections (Figure 5b). The cell membranes from oxidized wool also appear to be brittle and crack along straight edges, whereas the epicuticle tears along smooth curved lines.

An important problem is the chemical constitution of these cell membranes. Experiments on cell mem-



a

b



c

FIG. 4. *Cross sections of oxidized hairs treated with dilute ammonia. The oxidized keratin has entered solution, leaving the nonkeratinous residues.* a—*Human hair.* b—*Portion of whale hair.* c—*Wool fiber. In each case the cortical residue includes cell membranes, nuclear remnants (dark central areas in many cells) and a fine (particulate or rodlet) intracellular remnant distinct from the nucleus. This view of the cell membranes should be compared with that of Figure 2 to appreciate why they were mistaken for a distinct subcutis.*

branes of less specialized cells than those of hair show that such cells are usually clothed in extremely thin membranes composed of a protein and a lipoid in loose association. Possibly at their formation near the papilla of the hair follicle the presumptive cortical cells have such a membrane. It is possible, however, that this original membrane is toughened and thickened during the transformation of the cells into the horny formations of the final hair.

It is evident that the cell membranes still contain protein because they are digested by proteolytic enzymes. This was shown in the present experiments by introducing a few drops of trypsin to the cell cross sections after the ammonia extract had been washed away, and incubating at 40°C for 20 min. The cortical cell residues were quickly digested, leaving only a thin circle of the cuticular sheath. Stoves [30] and Hock, Ramsay, and Harris [13] have described similar observations. Moreover, in spite of intensive search, membranes other than the epicuticle are rarely found in enzymatic digestion of whole wool. The analytical work of Alexander and Earland [1] and of the present author has also demonstrated the presence of many amino acids in the residues.

X-ray examination of most of these resistant preparations usually yields a β-type pattern. The implication of this finding cannot be immediately accepted at its face value, owing to the possibility that some altered keratin may be present and responsible for the β-type diffraction pattern, but it offers further proof of a protein constituent.

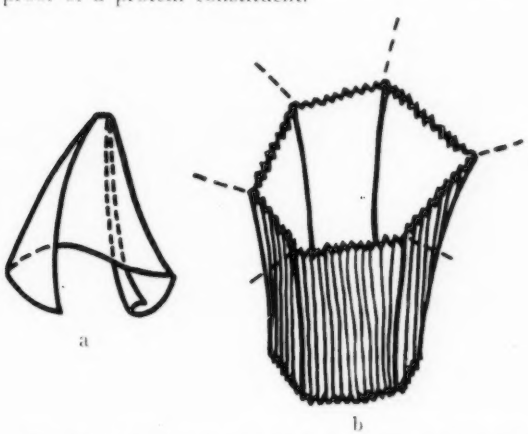


FIG. 5. *Sketches to emphasize characteristic features of the two kinds of membranes.* a—*Epicuticle: smooth, uniform, unwrinkled sheets with few broad folds.* b—*Cortical cell membranes: many fine, approximately parallel "pleats" or "gathers," as observed in the electron microscope.*

Minor Constituents

In addition to the cell membranes, two other kinds of resistant components were noted in treated sections. The first of these seem to be nuclear remnants; they are somewhat irregular, elongated forms centrally placed within the cell and visible in both side (Figure 2) and end (Figure 4) views of the sections. These structures have been separated and concentrated by fractional centrifugation, and will be discussed in a subsequent publication. Also interesting are the many particulate or short lengths of fibrils distributed throughout the volume of the cortical cells. In hair these are found uniformly in all cortical cells; in wool fibers, however, their distribution is asymmetrical—they occur in approximately one half of each cross section (Figure 4c). The implications of this structural asymmetry are discussed below.

The Asymmetry of the Cortex of Wool Fibers, Ortho- and Paracortex

The experiments described above suggest that in wool fibers the cortex may be divided into two halves differing in stability and other properties. Such a structural asymmetry may be demonstrated in other ways, and may be of considerable practical importance. Unsymmetrical dyeing (half-moon effects in cross section) is not uncommon [28] and, although usually attributed to uneven damage of the cuticle, may in fact have an original structural basis.*

The phenomenon of spontaneous twisting and curling is relevent here. Woods' study [31] of the geometry of crimp and the complex changes occurring on wetting fibers suggests that the geometrical form of a fiber is the result of a shifting equilibrium between several elastic elements which are unequally affected by the physicochemical environment. The same deduction may be made from the observations of Nitschke [27] and Berg [4], who studied the curling of fibers on steaming. Apart from suggesting that there are balanced elastic elements, these observations give no clue as to the level of organization (molecular, macromolecular, or histological) at which to look for the elastic elements. Harris [12] has proposed a balance between the contractile tendencies of cuticle and cortex, and this is possible, particularly in fibers having a thick cuticle.

Another type of experiment is that described by Freney [8], in which wool fibers are held stretched

* The very convincing experiments of Horio and Kondo [14] (this issue, p. 373) are of this nature.

and their spontaneous twisting and curling are noted. Freney described many complicated cycles of twisting and untwisting produced by changes in the environment. In conversation, Freney and the present author discussed the possible structural basis of these phenomena, without reaching a conclusion. A simple mechanical model possessing these properties is a composite rod formed by twisting together two hemicylinders of different materials; but microscopical evidence for such an asymmetrical formation, apart from the ambiguous evidence of partial dyeing, was lacking at that time.

The behavior of wool fibers oxidized with peracetic acid in alkaline solutions shows that an asymmetry does exist. In addition to the histological differences apparent in cross section (see above), the behavior of short lengths of fibers viewed longitudinally is significant. In 1% sodium bicarbonate the birefringence disappears more rapidly on one side of the fiber, and the short lengths usually curl into arcs. Further, in experiments based on the methods of Elöd and Zahn for the production of supercontracted fibers [7, 32]—*e.g.*, heating in formamide, aqueous phenol, and superheated water—it was found that lower temperatures and shorter times of treatment than those required to produce uniform contraction of the whole fiber produced an unsymmetrical contraction of one side of the fibers. The effect is best shown on short lengths when the loss of birefringence and lateral swelling on one side and curling are more readily seen (see Figure 6). The "contraction temperature" of protein fibers is usually taken as a measure of the stability of the fibrous system—*i.e.*, it is the temperature at which the thermal agitation of the long chains is sufficient to overcome the lateral forces (covalent cross-linkages, H-bonds, etc.) maintaining the ordered structure. That one half of the cortex of wool fibers is more readily contracted is therefore evidence of the lower stability of this section. The reason for this difference cannot be deduced immediately, since the cause could be molecular—*i.e.*, a greater degree of cross-bonding of the chains in the more stable section—or histological—*i.e.*, an admixture of a more stable reinforcing component, as might be deduced from the experiments with peracetic acid (see Figure 4c).

To facilitate subsequent discussion, the term "orthocortex" will be used for the less stable (ordinary) cortex, and "paracortex" for the portion of enhanced stability.

Methods of isolating comparatively pure paracortex have been developed from the fact that the cortical keratin after supercontraction becomes readily digested by trypsin, whereas uncontracted cortex is very resistant. Several methods of inducing unsymmetrical supercontraction have been tried, and the most uniform product was obtained from fibers contracted in superheated water, as follows (see Figure 6): (*a*) a fine merino wool was solvent-scoured, washed with water, and comminuted in a Wiley mill—the chopped fragments were about 1–2 mm. long; (*b*) the chopped wool was heated in a sealed vessel with water at 120°C for 1½ hrs.; (*c*) the fiber mass was then removed and treated with a trypsin solution (pH 8.6, 40°C) for 24 hrs. The course of digestion was checked microscopically, and the removal of the nonbirefringent, supercontracted orthocortex was followed. Prolonged digestion for several days does not remove the uncontracted paracortex.

The final preparation (see Figure 3) after 24 hrs. digestion consists of the cuticular sheath (*c.s.*) and the paracortex (*parac.*). The paracortex twists from side to side within the sheath in a spiral probably related to its original form in the whole fiber.

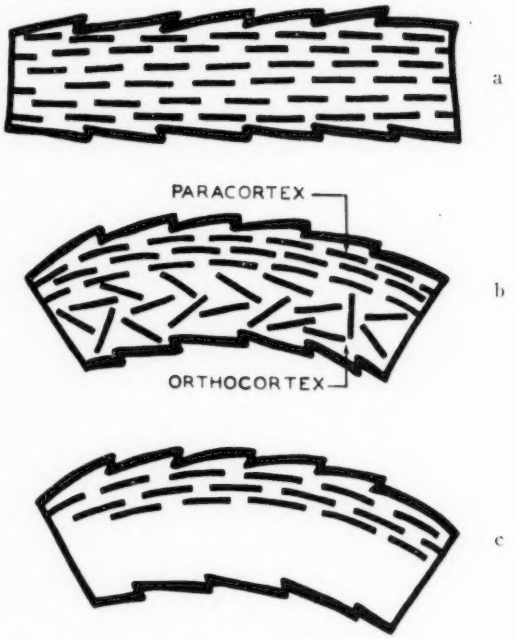


FIG. 6. *Sketch illustrating the differentiation of orthocortex and paracortex by unsymmetrical supercontraction* (b), *and the removal of the orthocortex by tryptic digestion* (c); (a) *is the original fiber.*

The paracortex prepared in this way may be stained with both acidic and basic dyes, but accepts the acid dyes more readily.

Attempts to free the paracortex from the sheath (less than 5% of whole) in order to obtain the analysis of the single component are in progress. Until an analysis is available to show whether a chemical difference exists between para- and orthocortex, discussion of the cause of their differences in stability would not be very profitable. Whatever the chemical differences, they seem to be evidenced at the histological level by the presence of a greater proportion of "nonkeratinous" constituents in the paracortex and by a relative difference in affinity for acidic and basic dyes—the paracortex being the more acidophilous, the orthocortex the more basophilous.

A study of the geometry of the isolated paracortex within the cuticular sheath shows that the paracortex and orthocortex form two approximately equal hemicylinders which are twisted together to form the total cortex. To judge from isolation experiments, the paracortex is somewhat smaller than the orthocortex, but staining experiments suggest that they are more nearly equal. The boundary line between the two sections is sharp, and seems to follow the cortical cell boundaries—*i.e.*, a cortical cell belongs entirely to one cortical type or to the other (see Figure 4c).

There seems little doubt that the twisted internal structure of the cortex is related to the external crimped form of the fiber. Wool is unique with respect to its finely crimped character, and no evidence of an unsymmetrical cortex has been found in hairs other than wool. The primary shape of the wool fiber undoubtedly has its origin in the twisted follicle in which the fiber grows,* and the unsymmetrical internal structure of the cortex should also be related to events within the follicle. The work of Auber [3] has shown that in most wool follicles the onset of keratinization in the cortex is unsymmetrical, occurring first on the side of the follicle having the thinner outer root sheath, leading to what Auber calls "segmental keratinization." It is possible that this original asymmetry at the onset of the hardening process may be responsible for the lack of symmetry in the degree of hardening and stability of the final fiber.

* This remark does not contradict the opinions of Horio and Kondo [14], who are more concerned with the way in which the primary follicular curl of the fiber is deformed extrafollicularly in the assembly of fibers forming the fleece to give the quasi-uniformly crimped staple.

Since the two parts of the cortex behave differently towards reagents, it is very probable that together they form the mechanism responsible for the spontaneous change in form of wool fibers which follows an environmental change. Woods [31] demonstrated a substantial difference between the coefficients of longitudinal expansion on the two sides of a fiber. The effects of this tendency to curl and uncurl may be apparent in the aging of wool during manufacture, in felting [12], and in the valuable tendency of woolen fabrics to retain "fullness" in wear. The desirability of investigating further the causes of the differences between the para- and orthocortex is obvious.

The Medulla

The medulla occurs rarely in fine wools and hairs, and for this reason little attention has been paid to its composition. There are, however, some chemical similarities between the resistant constituents of the cortex and those of the medulla which are of interest from our present point of view.

The cells which form the medulla take their origin from the tip and upper sides of the papilla in broader follicles. They are usually cuboidal in shape, and retain this shape as they advance along the follicle. As the hair hardens, the contents of the medullary cells condense around the nuclei, forming a network of fibrillar structures and creating in the intercellular interstices a system of interconnecting cavities.

When first formed, these cells do not differ in any obvious way from those destined to form the cortex. In fact, in fibers with an intermittent medulla, cells from the same point of origin may at one time become medullary cells and at other times cortical cells. The difference, appearing subsequently, is that in the typical cortical cell the intercellular synthesis of fibrous keratin fills the entire cell body with fibrils, whereas in the medullary cell such synthesis fails to occur. In a limited sense, then, the medullary cell may be expected to contain most of the cell constituents also found in the cortical cell, with the exception of the keratin. The chemical resistance of the contents of the medulla is similar to that of the nonkeratinous constituents of the cortex. The alkali resistance is high, as illustrated by the method of isolating medullary cells by warming hairs in strong caustic soda solution. Similarly, when medullated fibers are oxidized with peracetic acid or reduced with thioglycolic acid and then extracted with alkali, the medulla does not dissolve, but remains as

a residue along with the cuticular sheath and the cortical cell membranes. The medulla is also digested by enzymes. It would seem likely that a similarity in chemical structure is responsible for these similar solubility properties.

The medulla, when isolated by destroying chemically the rest of the fiber or separated by mechanical means from very coarse bristles or spines, is found to yield a poorly defined β-type x-ray pattern in which certain spacings (4.2 Å.), which are usually attributed to lipoids, are also prominent. Stoves isolated an unsaturated sterol [30]. Although the orientation as revealed by diffraction is poor, microscopic examination suggests that the major constituents are fibrous and that the local orientation in filamentous bundles or trabeculae is good. These fibrillar forms appear to result from a condensation of the intercellular bridges, which are prominent in the germinal layers of all epidermal tissues but which are obscured by the later development of keratin. Zahn and Haselmann [33], following Kuntzel, suggested that these "bridges" may persist also in the cortex and may help to link the cortical cells. These may form the apparently fibrous residuals found in the cortical cells after the removal of the keratin, whose identity (discussed above) is unsettled.

Other Keratinized Tissues

Other keratinized epidermal appendages consist of cells which are essentially homologous to the cortical cells of hair. A series of these materials, selected to cover broadly the range of types of tissue, has been examined to determine whether minor constituents, such as cell walls and nuclear remnants with properties similar to those found in hair, are present. Specimens of the following materials were cut into small pieces, extracted with boiling toluene for 6 hrs., and oxidized in 2% peracetic acid for 24 hrs.: human nails, skin, and calluses; horse's hoof; lion's claw; whale bone (baleen); chicken feathers; and rhinoceros horn. The oxidized materials were then placed in $M/100$ aqueous ammonia for 6 hrs., fragmented mechanically, stained with methylene blue, and examined microscopically.

All the oxidized material swelled greatly in ammonia, and microscopically were seen to consist of discrete cells whose walls and nuclei were well-defined. Ill-defined, undissolved material, also stained by methylene blue, was also noted in the cellular cavities.

These observations show that the conclusions relating to hair described above are of general significance.

Note on Enzymic Digestion of Hair

Certain preparative procedures involving enzymes are commonly employed to isolate components of hair for microscopic examination. Their success is based on the different rates at which the various components are digested by proteases.

The most resistant component is the epicuticle. Owing to its external position, it seems to be responsible in part for the slow digestion of the intact fiber since digestion proceeds most rapidly at cut ends and abrasions. When separated from the fiber by chlorination or bromination, this membrane is so altered that it is digestible. When digestion is accelerated by the addition of urea to the solution [17], the epicuticular residue is extensively pock-holed, showing that digestion is proceeding slowly.

The cell membranes and a certain amount of ill-defined cementing material are the most rapidly digested fractions of whole hair. Definite cell membranes have never been found in enzymic digests, in spite of an extensive search. The spindle-shaped bodies usually described as "cortical cells" are really cells stripped of their enveloping membranes and further "etched" by the enzyme.

The fibrous contents of the cortical cells are almost indefinitely resistant to trypsin and pepsin. It seems correct to ascribe this resistance to the compact, condensed molecular structure maintained largely by disulfide cross-linking. Rupture of the disulfide bonds by reduction [9] or by oxidation leads to easily digested derivatives. As intermediates in the digestion of such altered keratins, one may isolate macrofibrils and microfibrils and less well-defined particulate forms resulting from the disintegration of the fibrils. From the cuticle, tubules of various thicknesses down to the epicuticle alone result. Fully supercontracted cortex is rapidly digested, leaving empty cuticular sheaths. Unsymmetrical contraction of wool (see above) leads to the digestion of the orthocortex, leaving the paracortex.

Summary

A distinction has been made between keratinous and nonkeratinous constituents of hair and wool. The keratin may be removed in various ways after the stabilizing disulfide cross-linkages are broken,

leaving a nonkeratinous fraction which consists of (*a*) the thin epicuticle external to the scales, (*b*) the cell membranes of the cortical cells, (*c*) nuclear remnants, and (*d*) ill-defined particulate forms within the cortical cells.

The cortical cell membranes have hitherto been mistaken for a definite subcutis lying between the cuticle and cortex.

The resistant particles or short sections of fibrils noted in the cortical cells occur in only half of the cells in cross sections of fine wool. This asymmetry may be related to a relative difference in stability between one half of the cortex (orthocortex) and the other half (paracortex). The ortho- and paracortex form two twisted hemicylinders, and their different response to environmental changes may be responsible for the spontaneous twisting and curling of wool.

Other keratinized tissues contain similar resistant constituents.

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Relation Between Dyeing Properties of Wool and Modifications of the Fiber

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Abstract

Dye rates were measured for unsteamed and steamed solvent-extracted wool. These measurements indicate that the dye rates for wool that has not been alkali-damaged, or wool in which the alkali damage has been restricted to the fiber surface, are not influenced by steaming. The dyeing time for wool treated with an aqueous alkaline solution is increased considerably by steaming. This would indicate that the effect of steaming is due to modifications in the bulk of the wool fiber.

Introduction

During the last few years attention has been focused on the importance of the surface properties of the wool fiber in determining the physical, chemical, and technological behavior of the material. Freney and Lipson [1] showed that alcoholic potash remarkably influences the dyeing and felting properties of the fiber. Lindberg, Mercer, Philip, and Gralén [6] attributed these changes to an alteration of the surface layer, the "epicuticle." The action of alkali on the structure of the epicuticle was further studied with the electron-microscope by Lagermalm and Philip [2]. Lindberg has recently studied more extensively the effect of alcoholic potash treatment on various physicochemical properties of wool [3, 4, 5]. From these publications it can be seen that it is possible to change the dyeing and felting properties of the fiber by an attack which is restricted to the surface layers and which does not affect the bulk of the fiber.

O'Reilly *et al.* [7] in a recent publication dealt with the modification of the fiber surface during worsted processing, as indicated by sensitivity to the Pauly staining test and dye exhaustion rates.

Significant reductions in the sensitivity to the Pauly test and dye exhaustion rates were observed after steaming the material. Two hypotheses were proposed to explain this behavior: (*1*) there is an apparent healing of the damaged epicuticle upon steaming; and (*2*) in the steaming process the scales, distended in previous processing, tend to resume their original position.

O'Reilly *et al.* concluded that the position of the scales is the paramount factor, while they regarded as unlikely a healing of the damaged epicuticle upon steaming. They also suggested that "the epicuticle may actually surround each scale individually and leave some uncovered areas beneath the scales through which dye could easily penetrate when the scale is lifted."

Raising the scales would cause an increase in the available surface. This increase, however, could not be of an order of magnitude sufficient to account fully for the changes in dyeing rate caused by steaming.

The concept of the apparent healing of the damaged epicuticle warrants further consideration. This apparent healing effect may be that of a true restoration of the original structure of the epicuticle, or merely a masking of its "wounds" by swelling upon steaming and contraction during the subsequent cooling and drying of the fiber. In the latter case, further mechanical processing should once more open the "wounds" and produce an increase in the dye rate. Such an increase was found in the work done at Textile Research Institute.

This paper is the result of further investigation of the effect of steaming on the dyeing properties of the wool fiber.

Experimental

Dyeing experiments were made on a 64's wool which had been solvent-extracted and processed into top. In order to produce a uniform alkali damage

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restricted to the surface layer, the wool was treated with alcoholic KOH (2 g. KOH, 96 ml. 100% ethyl alcohol, 4 ml. distilled water) for 15 min. The excess alkali was neutralized. For details of these procedures and of the dyeing the reader is referred to the publication by Lindberg [5], who used the same material for his investigations.

The material to be steamed was placed in a glass tube through which steam was passed. In order to prevent condensation of the steam in the wool and on the tube, the tube was jacketed and steam was passed through the jacket, thus preheating the wool and tube and ensuring that the subsequent steaming of the material would be dry. The time of steaming was 15 min. in all cases.

One gram of the fibers was cut in short lengths (2–4 mm.), thoroughly wetted in a glass tube, and plunged into a dye bath of 800 ml. (0.1 g./l.), which was stirred rapidly. The dye used was Napthalene Scarlet 4 R 120 (I.C.I. color index 185). The bath was buffered to pH 3.5 (acetate buffer) and the dyeing temperature was 60°C.

The half-dyeing time (the time at which the concentration of the bath is reduced to one-half its original concentration) was used as the standard in measuring the dye sorption rates. The concentration of the dye in the bath was measured colorimetrically, using the equipment described by Lindberg [5]. First, a complete dye run was made, and 10-ml. aliquots of dye liquor were tested every 5 min. to obtain the approximate half-dyeing time. Then another run was made in which aliquots of the dye liquor were examined at shorter intervals near the half-dyeing time, thus enabling a more accurate estimate of this value to be obtained.

The results are given in Table I. It is evident that a treatment with alcoholic KOH reduces the half-dyeing time considerably. It is evident, also, that subsequent steaming does not restore the epicuticle, as it produces no significant increase in the half-dyeing time.

TABLE I

Treatment*	Half-dyeing time (min.) Unsteamed	Steamed†
EA	23	21
EA + KOH (15 min.)	3.2	2.5 (wet steam)
		3.5 (dry steam)
EA + pH 11	5.0	9.0
EA + pH 11 + KOH (4 min.)	3.3	4.7

* EA means extracted with ether and alcohol; KOH means treated with alcoholic KOH; pH 11 means treated with a solution of pH 11.

† When not otherwise stated, the steaming was with dry steam.

A scouring process, such as the one used in the Wool Research Project of Textile Research Institute, involves treatment of the wool with an aqueous alkaline medium. In order to study the influence of an aqueous alkaline medium, the alcoholic KOH treatment was replaced by immersion of the fibers in a buffer solution of pH 11 (nine parts of Na_2CO_3 and 1 part of $NaHCO_3$). The temperature was 50°C and time of immersion 30 min.

This treatment did not reduce the half-dyeing time for the unsteamed sample to the same extent as a 15-min. treatment with alcoholic KOH. However, an appreciable reduction was obtained. Subsequent steaming almost doubled the half-dyeing time. This is in line with the results reported by O'Reilly *et al.*, but the effect is even more pronounced.

If the wool is treated first with an aqueous bath at pH 11 and then, after conditioning, with alcoholic KOH, the half-dyeing time for the unsteamed sample is approximately the same as that for the unsteamed sample treated with alcoholic KOH alone. However, after steaming, the sample subjected to both the pH 11 and alcoholic KOH treatments has a half-dyeing time which is shorter than that for the steamed sample pretreated with aqueous alkali.

Swelling Experiments

The dyeing experiments show that the epicuticle is not responsible for the effect of the steaming. In order to study the influence of steaming on a typical bulk property, swelling experiments were made.

Samples weighing about 1 g. were immersed for 1 hr. in distilled water containing a small amount of a wetting agent to reduce the surface tension. The samples were then centrifuged for 15 min. at 1,000 g., immediately weighed, dried for ½ hr. at 105°C, and weighed again. The swelling is expressed as the percentage of water held, based on the dry weight.

TABLE II

Treatment*	Swelling (% water†) Unsteamed	Steamed
EA	33.1	31.6
EA + pH 11	36.3	33.1
EA + pH 11 + KOH (4 min.)	37.1	34.7

* Same code as in Table I.

† Calculated on dry-weight basis.

It can be seen from Table II that the difference in the swelling properties before and after the steaming is greatest when the fibers had been treated with the solution of pH 11. The influence of steaming on swelling is significant, but the experimental data is too scanty to justify more detailed conclusions.

An additional treatment with alcoholic KOH does not influence the results, and Lindberg [3] has shown that treatment with alcoholic potash alone does not change the swelling properties of the fibers.

Discussion

Dyeing experiments have shown that the epicuticle largely controls the rate of sorption. Patchy staining and tippy dyeing indicate that this rate is different in different parts of the fiber. The dye will be sorbed largely through the parts of the surface where the epicuticle is damaged. As long as the damage of the fiber is restricted to the epicuticle, steaming does not affect the dye rates to any significant degree. Thus, steaming does not cause a restoration of the original state of the epicuticle, and from the evidence of the dyeing and swelling experiments we conclude that the bulk of the fiber is responsible for the effect obtained by steaming.

The distribution of the dye throughout the bulk of the fiber will depend upon the rate of diffusion in the bulk structure. The total rate of sorption will be dependent upon both the extent of irreversible damage of the epicuticle, which is related to the available surface for dye penetration, and the properties of the bulk structure, which evidently can be reversibly modified by aqueous alkaline treatment and steaming. A detailed theory, including a mathematical treatment of the factors involved in this mechanism, is given elsewhere by Lindberg [5].

As shown in Table I, the epicuticle can be damaged to varying degrees. This damage may be combined with a modification of the bulk properties, or done in such a way as not to affect them at all. Thus, it should be possible to obtain a better control of the dyeing process.

O'Reilly *et al.* reported an increase in the surface modifications with progressive processing. In their paper, the position of the scales was related to the extent of dye susceptibility. In order to mechanically damage the solvent-extracted wool used for our experiments, a sample was hand-carded several times and rolled between gears. The sample had not been alkali-treated in any way. Microscopical observations did not reveal any significant changes in the surface structure, nor did the treatment produce any change in half-dyeing time. Probably this mechanical treatment is not comparable to that encountered in processing, and since the experimental evidence regarding this is too scanty, it is not included in Table I. It does not seem unlikely, however, that alkali-scoured wool may have a higher sensitivity to surface modifications caused by mechanical treatment than solvent-extracted wool.

The possibility still remains that the distention of the scales, with an accompanying increase in surface and opening of all "wounds" to dye diffusion, may play some role. A microscopical investigation of the samples subjected to the various physical and chemical treatments, however, failed to show any distention of scales. This factor is thought, therefore, to be of minor importance compared to the influence of the bulk of the fiber.

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The Analysis of Cotton-Glass-Asbestos Yarn

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Contribution from the General Laboratories of the United States Rubber Company, Passaic, New Jersey

ALTHOUGH there are several methods for analysis of mixtures of cotton and asbestos in yarns, no satisfactory method has been available for the analysis of yarns containing glass as an additional component. The method described in this paper is designed to permit analysis for all three components in the simplest possible manner. Lloyd and Priestly [7] separated cotton from asbestos by solution in 35% sulfuric acid. Lukens [9] determined asbestos by loss of weight on ignition. Heermann and Sommer [5] dissolved the cellulose with Kuoxam solution. Sommer [11] later surveyed the field and stated that the Kuoxam method was the only satisfactory one for this analysis. Wilmet and Reglade [13] oxidized the cellulose to carbon dioxide, which was then determined titrimetrically. Most of the recent literature concerning the determination of cellulose refers to the spectrophotometric method involving the reaction of anthrone with cellulose [2, 3, 8, 10, 12]. This method has been shown to be quite satisfactory for those laboratories which have facilities for spectrophotometric analysis. However, a much more simple method has been developed in this laboratory. The method involves simple carbon, hydrogen, and ash determinations after careful preparation of the sample.

Theory

Since the least variable component of Canadian asbestos (Chrysotile) is the water of crystallization and/or constitution (see Table I), the A.S.T.M. method for the determination of asbestos in yarns containing only cotton and asbestos [1] involves only an ash determination. The analysis is based on the fact that a large number of Chrysotile samples yielded an average water content of approximately 14%. Thus, 86% of the asbestos will remain as ash while all of the cotton should be burned away.

Inasmuch as virtually all of the glass fibers used in making a cotton-glass-asbestos yarn should remain as ash, the analysis of such a yarn can be accomplished by simple carbon, hydrogen, and ash determinations. The carbon content can be used to determine the amount of cotton present, since the only source of carbon in a cotton-glass-asbestos yarn is the cotton. The hydrogen content indicates the amount of asbestos present, since all hydrogen not arising from the cotton should come from the asbestos. Having determined the cotton and asbestos contents, the glass content can then be determined by means of the ash content. The ash, of course, should be composed of virtually all of the glass, 86% of the asbestos, and none of the cotton.

TABLE I. COMPOSITION OF CHRYSOTILE

Component	Range of values	Deviation (lower and higher values) (relative)
Water	13.38%–13.80%	about 3%
MgO	40.76%–43.70%	about 7%
Silica	38.45%–43.36%	about 13%
Alumina	up to 1%	over 100%
Ferrous oxide	up to 2.05%	over 100%
Ferric oxide	up to 4.25%	over 100%

Development of the Equations

% Cotton

Table II shows the results of carbon, hydrogen, and ash determinations on a typical cotton yarn.

The % cotton then equals 1/.4349 times the % carbon. The value for % carbon must first be corrected for small amounts of carbon arising from glass

TABLE II. ANALYSIS OF A COTTON YARN

Run	Carbon (%)	Hydrogen (%)	Ash (%)
1	43.37	6.27	1.41
2	43.39	6.30	1.15
3	43.54	6.29	1.13
4	43.52	6.27	1.19
5	43.52	6.29	1.39
6	43.58	6.29	1.25
Average	43.49	6.29	1.25

and asbestos:

$$\% \text{ Cotton} = \frac{1}{.4349}(\text{total carbon} - .007 \times \%\text{asbestos} - .007 \times \%\text{glass})$$
$$= 2.30 \times \%\text{carbon} - .0161\,(\%\text{asbestos} + \%\text{glass}). \quad (1)$$

In the event that the cotton value is too high to meet specifications, it may be checked by the anthrone method.

If mineral carbonates are present, they may be determined separately by the Knorr method [6] and the necessary corrections made.

% Glass

Table III shows the results of carbon, hydrogen, and ash determinations on a typical sample of glass fibers.

The % glass then equals 1/.9861 times the % ash. The value for % ash must first be corrected for the ash arising from cotton and asbestos:

$$\% \text{ Glass} = \frac{1}{.9861}(\text{total ash} - 0.0125 \times \%\text{cotton} - .8754 \times \%\text{asbestos})$$
$$= 1.014 \times \%\text{ash} - .01267 \times \%\text{cotton} - .8876 \times \%\text{asbestos}. \quad (2)$$

% Asbestos

Table IV shows the results of carbon, hydrogen, and ash determinations on a typical sample of Chrysotile asbestos.

The % asbestos equals 1/.0154 times the % hydrogen (after correction for the hydrogen from cotton and glass):

$$\% \text{ Asbestos} = \frac{1}{.0154}(\%\text{hydrogen} - .0629 \times \%\text{cotton} - .0015 \times \%\text{glass})$$
$$= 64.93 \times \%\text{hydrogen} - 4.09 \times \%\text{cotton} - .097 \times \%\text{glass}. \quad (3)$$

TABLE III. ANALYSIS OF GLASS

Run	Carbon (%)	Hydrogen (%)	Ash (%)
1	0.70	0.21	98.84
2	0.61	0.09	98.67
3	0.77	0.12	98.67
4	0.71	0.28	98.62
5	0.71	0.05	98.23
Average	0.70	0.15	98.61

Solving the Equations

Solving these three equations can best be accomplished by assuming that the mixture is made up entirely of cotton, glass, and asbestos.

Let x = % cotton, y = % glass, z = % asbestos:

$$x + y + z = 100$$
$$(y + z) = 100 - x.$$

Equations (1), (2), and (3) then become:

$$x = 2.30 \times \%\text{carbon} - .0161\,(y + z) \quad (4)$$
$$y = 1.014 \times \%\text{ash} - .01267x - .8876z \quad (5)$$
$$z = 64.93 \times \%\text{hydrogen} - 4.09x - .097y \quad (6)$$

The % cotton can be calculated from the carbon content by combining equation (4) and the equation $x + y + z = 100$. Then

$$x = 2.30 \times \%\text{carbon} - .0161\,(100 - x)$$
$$.9839x = 2.30 \times \%\text{carbon} - 1.61$$
$$x = 2.34 \times \%\text{carbon} - 1.64. \quad (7)$$

By substituting the above value for x in equations (5) and (6), these equations can be solved simultaneously:

$$y = 1.014 \times \%\text{ash} - .01267\,(2.34 \times \%\text{carbon} - 1.64) - .8876z$$
$$z = 64.93 \times \%\text{hydrogen} - 4.09\,(2.34 \times \%\text{carbon} - 1.64) - .097y.$$

By rearranging the first of these equations and carrying out the indicated multiplications, we have:

$$.8876z = 1.014 \times \%\text{ash} - .0296 \times \%\text{carbon} + .0208 - y$$
$$z = 64.93 \times \%\text{hydrogen} - 9.57 \times \%\text{carbon} + 6.71 - .097y.$$

Solving for y:

$$y = 1.11 \times \%\text{ash} - 63.05 \times \%\text{hydrogen} + 9.26 \times \%\text{carbon} - 6.50. \quad (8)$$

Solving for z:

$$z = 71.05 \times \%\text{hydrogen} - 10.47 \times \%\text{carbon} + 7.34 - 0.11 \times \%\text{ash}. \quad (9)$$

TABLE IV. ANALYSIS OF ASBESTOS

Run	Carbon (%)	Hydrogen (%)	Ash (%)
1	0.33	1.41	87.77
2	0.27	1.44	87.73
3	0.67	1.51	87.74
4	0.79	1.60	87.47
5	1.05	1.60	87.27
6	1.07	1.69	87.26
Average	0.70	1.54	87.54

TABLE V. ANALYSIS OF COTTON-GLASS-ASBESTOS

Sample	Carbon (%)	Hydrogen (%)	Ash (%)
A	8.78	2.37	71.05
	8.29	2.33	72.29
	8.68	2.36	71.43
	8.26	2.32	72.34
Average	8.50	2.35	71.63
B	6.89	2.07	75.64
	7.07	2.10	75.68
	6.66	2.06	75.90
Average	6.87	2.08	75.74

Procedure

The sample is pulverized using a Wiley mill, which assures homogeneity of the sample. It is then extracted with ether (or chloroform) using a Soxhlet extractor. At the end of a 4-hr. reflux period, the sample is removed from the extractor and the excess solvent is allowed to evaporate. The sample is then dried at 105°C for a period of at least 2 hrs. It is allowed to come to room temperature in a desiccator for a period of ½ hr. (or until constant weight is obtained).

An accurately weighed sample of approximately 0.600 g. is carefully packed into the combustion boat for carbon, hydrogen, and ash determinations. This is a considerably larger sample than usual in order to increase the accuracy of the hydrogen and ash determinations. An excellent discussion of the method, including setting up of the apparatus, may be found in Fisher's *Laboratory Manual of Organic Chemistry* [4].*†

* Anhydrone is used in the first absorption tube to absorb the water formed in the combustion.

† The cerium oxide portion of the combustion tube filling is replaced by a copper oxide wire spiral.

By eliminating the copper oxide spiral between the source of oxygen and the combustion boat, the ash determination can be made on the same sample as was used for carbon and hydrogen analyses merely by weighing the boat after completion of the carbon and hydrogen determinations. The elimination of the wire spiral decreases the danger of contamination of the boat by particles of copper oxide.

The cotton, glass, and asbestos contents are calculated from equations (7), (8), and (9), respectively.

Results

Table V gives the results of carbon, hydrogen, and ash determinations on two samples of cotton-glass-asbestos yarns. Sample *A* was formulated to contain 70% asbestos, 20% cotton, and 10% glass. Sample *B* was of unknown fiber content.

Table VI gives the results of the analysis of the cotton-glass-asbestos yarns for the three components.

Anthrone Method

In order to check the value obtained for the cotton content of the two yarns, the anthrone method was utilized. A slight modification of the procedure of Black [2] was required. Briefly, the method used was as follows:

Reagent

0.30 g. of anthrone was put into 75 ml. of ordinary concentrated sulfuric acid in a 500-ml. volumetric flask. To this solution was added 200 ml. of 71.0% (by weight) sulfuric acid. A 150-ml. portion of 71% acid was then added with 50 ml. of water (caution). The solution was cooled and diluted to 500 ml.

TABLE VI. ANALYSIS OF COTTON-GLASS-ASBESTOS YARNS FOR THE THREE COMPONENTS

Sample	Cotton (%)	Deviation (absolute) (%)	Glass (%)	Deviation (absolute) (%)	Asbestos (%)	Deviation (absolute) (%)	Total
A	18.91	0.65	4.24	0.18	75.98	1.06	99.13
	17.76	0.50	3.60	0.46	78.14	1.10	99.50
	18.67	0.41	4.37	0.31	86.28	0.76	99.32
	17.69	0.57	4.01	0.05	77.74	0.70	99.44
Average	18.26	0.53	4.06	0.25	77.04	0.90	99.35
B	14.48	0.04	10.75	0.47	73.95	0.62	99.18
	14.90	0.46	10.56	0.28	74.21	0.36	99.67
	13.94	0.50	9.54	0.76	75.62	1.05	99.10
Average	14.44	0.33	10.28	0.50	74.57	0.68	99.32

TABLE VII. CELLULOSE BY ANTHRONE METHOD

Cellulose taken (mg.)	Cellulose found (%)		Error (%)
0.100	0.100		0.00
0.100	0.105		5.00
0.195	0.196		0.51
0.195	0.200		2.55
0.390	0.393		0.77
0.390	0.387		0.77
0.500	0.505		1.00
0.500	0.507		1.40
0.700	0.696		0.57
0.700	0.696		0.57
		Average	1.31

TABLE VIII. COTTON BY ANTHRONE METHOD

Sample	Cotton (anthrone) (%)	Cotton (C & H) (average) (%)	Deviation from value derived from C & H value (%)
A	17.99	18.26	1.48
	18.06	18.26	1.09
	18.06	18.26	1.09
	17.99	18.26	1.48
			Average 1.29 (relative)
B	14.20	14.44	1.67
	13.90	14.44	3.74
	14.01	14.44	2.99
	14.08	14.44	2.49
			Average 2.72 (relative)

Standard

Whatman No. 2 filter paper was cut into squares 23 mm. on a side (dry weight, about 50 mg.), and dried at 105°C for 2 hrs. before weighing. One square of this standard was dissolved in 150 ml. of 71% sulfuric acid in a 250-ml. volumetric flask. The solution was diluted to mark with 71% sulfuric acid.

Procedure

Dissolve a weighed amount of cellulose (cotton, rayon, paper, etc.) in a measured volume of 71% sulfuric acid. The weight is chosen so that a 10-ml. aliquot will contain about 0.5 mg. of cellulose. Take a 10-ml. aliquot of the sample and transfer to a 50-ml. volumetric flask. Add 30 ml. of the anthrone reagent. Place in boiling water for *exactly* 15 min. (one minute more or less makes a 2% relative error). Cool to room temperature and measure the absorbance (optical density) at 627.5 millimicrons using a Beckman Model DU Spectrophotometer. Calculate the % cellulose.

Results

Table VII shows the results obtained with known amounts of cellulose, and Table VIII shows the results obtained with the two samples of cotton-glass-asbestos yarns. The % cotton values were obtained by dividing the % cellulose by 0.98 to account for the fact that cotton is only about 98% cellulose.

Summary

A method of analysis has been developed for the determination of cotton-glass-asbestos yarns. The method is based on a simple carbon, hydrogen, and ash determinations after extraction of finishing agents from the sample. The precision on the samples thus far investigated has been approximately ± 3% (relative) for cotton, 5% for glass, and 1% for asbestos. The precision of these determinations appears to be considerably better than could be obtained by any other method for the three components in a mixture.

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The Tensile Behavior of Some Protein Fibers*

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Abstract

The tensile properties of wool, mohair, human hair, casein, Vicara, and silk, including their behavior when knotted, after repeated stresses (mechanical conditioning) and when swollen in water were investigated. The immediate elastic recovery, the delayed recovery, and the permanent set of these fibers were measured by means of a cycling technique using the Instron tensile tester and the Sookne-Harris fiber extensometer. Actual and relative values of elongation components under different testing conditions are demonstrated graphically from the beginning of the stretching procedure up to rupture.

Wool has an outstanding elastic recovery in the dry state, and its elastic behavior is improved after mechanical conditioning and when wet. Mohair and human hair, and to some extent casein and Vicara, have elastic properties similar to those of wool. The tensile behavior of silk is different, being characterized by considerable permanent set (dry and wet) and by high immediate elastic recovery after mechanical conditioning.

WOOL is the most important protein fiber, and has a combination of extraordinary properties not found in any other natural, man-made, or synthetic textile material. The present study is confined to the tensile properties—*i.e.*, tenacity, extensibility, and elastic recovery—of wool and other protein fibers. Major emphasis is placed on recovery, since the high resilience of wool is partly responsible for its outstanding performance [4]. The behavior of wool is compared to that of five other natural and regenerated protein fibers: mohair, human hair, casein, Vicara [5], and silk. These fibers are similar to wool in that they consist of long-chain protein molecules, although some differences exist in their chemical composition, crystallinity, and crystal structure, and they are also considerably different in morphology. The aim of the present study is to learn to what extent wool-like tensile properties are present in these closely related fibers.

Test Methods

Tensile tests were made using two instruments: the Instron tensile tester, Model TT-B [1, 3], and the Sookne-Harris fiber tester [7, 8]. It is not surprising that results obtained by such different instruments deviate somewhat from each other, reflecting the particular conditions of the tests performed. These differences, however, were found to be relatively slight.

The stress-strain properties of fibers were tested first under standard conditions at 70°F (21.1°C) and 65% relative humidity. A 5-in. (12.7 cm.) gage length and a jaw separation rate of 5 in. (12.7 cm.) per min., corresponding to 100% elongation of the specimen per min., were used for the Instron tensile tester. Since these conditions could not be duplicated in the Sookne-Harris tester, the longest practical gage length, 2.0 in. (5.1 cm.), and the highest jaw speed, 0.2 in. (0.51 cm.) per min., corresponding to 10% elongation of the specimen per min., were used.

Stress-strain curves obtained under standard conditions reveal to only a limited extent the tensile behavior of fibers. Therefore, knot tests and tests after repeated stresses and when wet have been included in this study. Poor knot behavior is an indication of some inherent weakness of the fiber not observable on the conventional stress-strain curve. Knot tests also supply information on transverse properties, because they reflect the response of fibers not only to tension, but also to bending, compression, shear, and high-stress concentrations. The knots were overhand knots tightened mechanically by using the Instron tensile tester in order to improve the reproducibility (which would otherwise be rather low). An 8-in. (20.3 cm.) sample, loosely knotted,

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was first subjected to three consecutive loading cycles at a low jaw speed, 0.5 in. (1.27 cm.) per min., or 6.3% elongation per min., to a stress of 5% or 10% of the average breaking load, depending on fiber stiffness. This tension was sufficient to obtain a tight knot, but did not exceed the elastic limit.

Textile fibers in their practical use are almost always subjected to repeated stresses and strains which may substantially change their tensile properties. This alteration consists mainly in the elimination of permanent set, evidenced by a considerably lower extensibility after the fibers have been stressed or strained. Textile materials can react very differently after such "mechanical conditioning." The fibers were mechanically conditioned in the Instron tensile tester by extending them 50 times, from zero tension to an elongation level corresponding to 80% of their elongation at break, using an initial gage length of 8 in. (20.3 cm.) and a jaw movement of 5 in. (12.7 cm.) per min., or 62.5% elongation per min. The samples were allowed to relax for 1 hr. without tension after cycling to permit equilibrium to be attained before testing.

It is known that the tensile properties of protein fibers are markedly affected by changes in humidity and when swollen in water. Although tests were not made at various humidities, they were performed on wet fibers, which represent an extreme in moisture uptake. Tests of wet yarns were carried out with the Instron tensile tester after swelling in water for 1 hr. The swollen yarns were protected from drying during the test by means of a wet fabric cover entirely surrounding the specimen. Wet single fibers dried too quickly to permit testing by this technique. Single fibers were therefore tested immersed in water using the Sookne-Harris tester and slightly modified test conditions: gage length, 1.5 in. (3.8 cm.); jaw speed, 0.2 in. (0.51 cm.) per min., corresponding to 13.3% elongation per min.

A critical study of tensile behavior must include recovery, since it is necessary to know to what extent an imposed strain may recover when the tension is released. It is, of course, important to differentiate between that part of the elongation which recovers immediately and that which recovers after a longer relaxation period.

The recovery of protein fibers in the original state, after mechanical conditioning, and when wet was tested using a repeated-cycling technique, previously described [10], to separate three components of the total elongation: immediate elastic recovery, delayed recovery, and permanent set. Recovery tests of yarns were performed on 10 to 15 individual samples, each extended in the Instron tester to an increasing strain level. Immediate removal of the extension and a relaxation time of 5 min. were used. Under these conditions, immediate elastic recovery is that part of the total elongation which takes place in the range of a fraction of a second to a few seconds, according to the magnitude of the strain. Delayed recovery, or primary creep, is the additional recovery attained after a relaxation period of 5 min. Permanent set is that part of the total elongation which does not recover in 5 min. Some authors designate this component as "semi-permanent set," "temporary set," or "secondary creep." Only the recovery of wet single fibers was tested in the Sookne-Harris tester, in which one specimen was repeatedly extended to increasing strain levels up to the breaking point and then allowed to relax, but for only 1 min. These testing conditions were not as suitable as those used for the Instron tester, with the larger initial gage length and the higher speed of crosshead travel. In recovery tests using the cycling technique, the approximation of the true values of immediate recovery depends upon a sufficiently high jaw speed in the recovery cycle. This was 100% elongation per min. for the Instron, and only 13.3% for the Sookne-Harris tester. It is also obvious that data obtained on a set of samples, as practiced in tests with the Instron, are more representative.

The recovery behavior of fibers is demonstrated at different stress and strain levels either by actual values (% of the three elongation components correlated to the initial length) or by relative values (% of each elongation component correlated to the corresponding total elongation). Actual values are shown by four curves, and relative values by rectangular and quadratic graphs.

Fibers Tested

Eight protein fibers were investigated. Wool and mohair were tested both as single fibers and staple yarns, human hair and Vicara as single fibers, and casein and silk as multifilament yarns. The two latter samples reflect mainly fiber properties since multifilaments with low twist were tested.

Stress-Strain Properties of Fibers Tested

The stress-strain relationships for these fibers in the original state and when knotted are shown in Figure 1, after mechanical conditioning in Figure 2,

and when wet in Figure 3. The characteristics of the fibers tested and the ultimate values of the stress-strain curves represented in Figures 1, 2, and 3 are listed in Table I. The coefficients of variation of the ultimate points as obtained on 10 specimens indicate the uniformity of the samples and the reproducibility of tests.

Original Fibers

The following facts are apparent from the results shown in Figure 1: The stress-strain relationship, tenacity, and elongation at break of silk are different from those of the other protein fibers tested, as would be expected from the marked chemical differences (silk fibroin consists mainly of four amino acids without bulky side-chains, cross-linked by hydrogen bonds) and structural differences (high crystallinity, high orientation) which exist between them. The human hair sample is the strongest and the most extensible of the keratin fibers tested. Its elongation at break exceeds even the man-made protein fibers, casein and Vicara. The initial flat portion on the stress-strain curve for the wool single fiber and the slow increase of stress at the beginning of the stretching process reflect the crimp (approximately 4%). Such a flat portion is not apparent on the stress-strain curve for the wool yarn. The initial modulus, the yield point, and the tenacity at break for wool and mohair yarns are lower than the values for the corresponding single fibers, showing the influence of yarn structure. The low extensibility of the mohair yarn indicates slippage of single fibers as a result of the smooth surface, absence of crimp, and relatively low twist. A decrease of tenacity with increasing elongation after the yield point is passed is characteristic for the man-made fibers, casein and Vicara. This decrease is due to considerable "plastic flow," which is not present to such an extent in natural protein fibers.

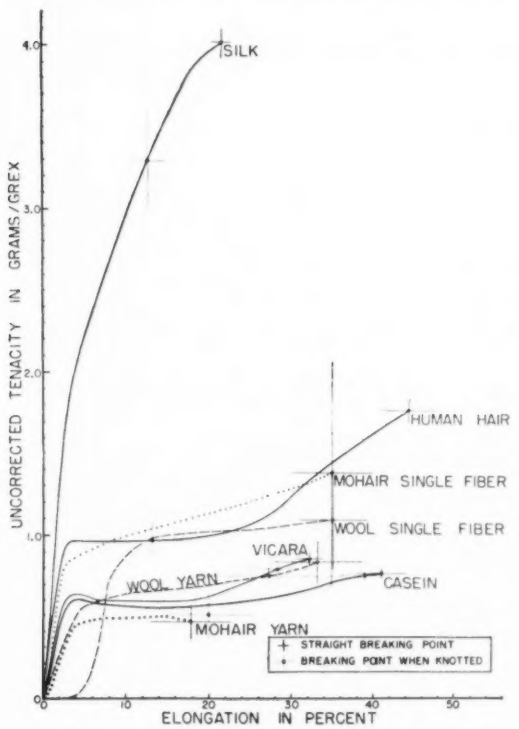

FIG. 1. *Stress-strain curves for original fibers. Vertical and horizontal lines indicate standard deviations of ultimate values.*

Effect of Knotting

Most of the specimens tested when knotted fail near the original breaking point. The wool staple yarn, the silk and casein multifilaments, and the Vicara single fiber have high relative knot tenacities —namely, between 82% and 98%. If both decrease of tenacity and extensibility are considered, only silk and human hair show appreciable losses when knotted. The low relative tenacity and extensibility for knotted human hair (54% and 30%, respectively) indicate a notable weakening, which is probably due to the large fiber diameter of 69 μ. The surprisingly high values for mohair yarn (108% and 111%, respectively) are a result of restricted slippage by the knot. The staple fibers are long, having an average length of 4.4 in. (11.2 cm.), and premature slippage is prevented by the presence of the knot under the conditions of the tests performed.

Effects of Mechanical Conditioning

The following five materials were tested after mechanical conditioning: single fibers of human hair and Vicara, multifilaments of silk and casein, and wool staple yarn.

A marked increase of the original fiber length and consequently a decrease in the fiber grex were observed in every case after repeated stresses. The stress-strain relationship of mechanically conditioned fibers is demonstrated in two ways: by correlating uncorrected tenacities to the original fineness before mechanical conditioning (Figure 2A), and to the

TABLE I. CHARACTERISTICS AND STRESS-STRAIN PROPERTIES OF FIBERS TESTED

	Wool single fiber	Worsted wool yarn 28.4/1	Mohair single fiber	Mohair yarn 28/1	Human hair single fiber	Casein multi-filament 300/40	Vicara single fiber	Silk multi-filament
Characteristics								
1. Original fineness (grex)	15.5	315	13.4	312	50.2	333	3.33	117
2. Staple length								
(a) in.	3.75	2.85	4.38	4.41				
(b) cm.	9.5	7.2	11.1	11.2				
3. Twist								
(a) turns/in.		20.9		16.0		4.5		4.1
(b) turns/cm.		8.2		6.3		1.8		1.6
4. Density	1.34	1.34	1.34	1.34	1.34	1.29	1.24	1.38
Original Behavior								
5. Tenacity at break								
(a) Uncorrected (g./gx.)	1.10*	0.84	1.39*	0.48	1.82	0.78	0.86	4.02
Coefficient of variation (%)	28.3*	15.5	53.0*	20.7	3.7	4.3	6.0	2.5
(b) Corrected (g./gx.)	1.44*	1.12	1.88*	0.56	2.63	1.10	1.14	4.89
6. Elongation at break (%)	31.0*[5]	33.2	35.0*	17.8	44.4	41.0	32.3	21.8
Coefficient of variation (%)	13.9*	17.2	15.0*	29.7	8.2	7.8	4.6	5.4
Knotted								
7. Tenacity at break								
(a) Uncorrected (g./gx.)		0.75		0.52	0.98	0.76	0.79	3.30
Coefficient of variation (%)		19.4		28.3	11.3	3.3	11.5	8.9
(b) Relative knot tenacity (%)		90		108	54	98	92	82
(c) Corrected (g./gx.)		0.86		0.62	1.15	1.06	0.91	3.71
8. (a) Elongation at break (%)		27.3		19.9	13.1	39.0	28.2	12.7
Coefficient of variation (%)		31.3		25.8	35.2	7.2	14.1	16.1
(b) Relative knot extensibility (%)		82		111	30	96	87	58
Mechanically Conditioned								
9. Increased length (%)[1]								
(a) Immediately		16.9			23.8	25.1	20.0	11.9
(b) After relaxation		10.6			21.2	23.8	17.5	11.2
10. Shrinkage (%) during relaxation[1]		6.3			2.6	1.3	2.5	0.7
11. New fineness (grex)		285			41.4	269	2.84	106
12. Tenacity at break								
(a) Uncorrected (g./gx.)[2]		0.82			1.79	0.82	1.02	3.98
Coefficient of variation (%)		8.7			5.3	3.9	13.3	3.4
(b) Uncorrected (g./gx.)[3]		0.91			2.17	1.02	1.20	4.40
(c) Corrected (g./gx.)		1.14			2.58	1.16	1.32	4.71
13. Elongation at break (%)[4]		25.3			18.9	13.7	10.1	7.0
Coefficient of variation (%)		17.5			6.8	11.5	16.3	11.8
Wet								
14. Tenacity at break								
(a) Uncorrected (g./gx.)	0.66*	0.48	1.14*		1.34*	0.28	0.61*	3.21
Coefficient of variation (%)	48.2*	13.1	29.4*		15.6*	7.3	21.0*	3.3
(b) Relative wet tenacity (%)	60*	58	83*		78*	36	68*	80
(c) Corrected (g./gx.)	0.96*	0.72	1.80*		2.02*	0.41	0.84*	4.27
15. (a) Elongation at break (%)	45.0*[5]	49.0	57.5*		51.3*	44.2	38.8*	33.1
Coefficient of variation (%)	15.8*	6.5	12.7*		12.6*	6.5	20.0*	4.4
(b) Relative wet extensibility (%)	145*	148	165*		116*	112	112*	151

[1] Correlated to the original length.
[2] Correlated to original fineness before mechanical conditioning (listed in line 1).
[3] Correlated to new fineness after mechanical conditioning (listed in line 11).
[4] Correlated to the new length after mechanical conditioning.
[5] Without crimp.
* Values obtained using the Sookne-Harris tester.

new fineness after mechanical conditioning (Figure 2B).

The uncorrected tenacities of mechanically conditioned fibers correlated to the new fiber fineness (line 12b, Table I) are always higher than the original tenacities (line 5a). Except for Vicara, practically identical values appear, however, when uncorrected tenacities of mechanically conditioned fibers correlated to the original fiber fineness (line 12a) or corrected tenacities (line 12c) are compared with the original tenacities (lines 5a and 5b). They show that no loss in tenacity occurred by mechanical conditioning (fatigue), despite the severity of the conditions under which the repeated extensions were performed. The higher tenacity of Vicara indicates a stress-hardening (approximately 17%), which is most likely the result of alignment of long-chain molecules in the amorphous and crystalline portions of this fiber. In contrast to this behavior, the extensibility of all the five fibers tested decreased markedly after mechanically conditioning (compare lines 6 and 13). This phenomenon was caused by the elimination of permanent set, as will be shown later in the investigation of recovery behavior.

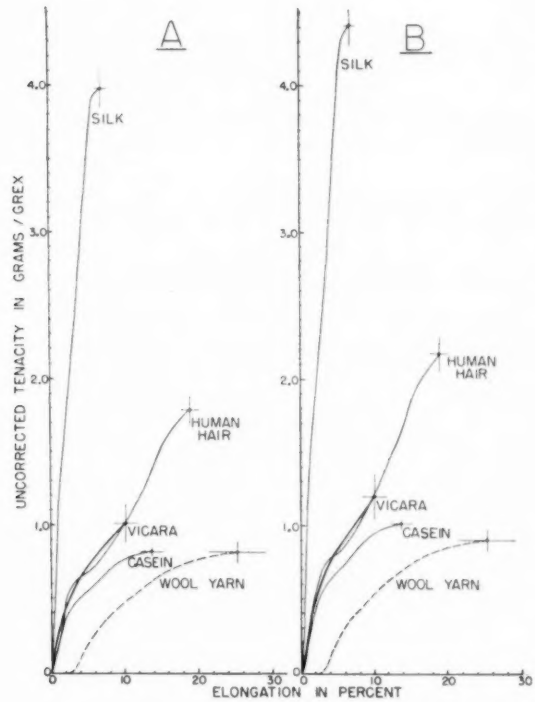

FIG. 2. *Stress-strain curves for mechanically conditioned fibers.* A—*Tenacity values based on original fineness.* B—*Tenacity values based on new fineness (after mechanical conditioning). Vertical and horizontal lines indicate standard deviations of ultimate values.*

After repeated stresses the definite yield point disappeared from the stress-strain curves of wool and Vicara, and was barely perceptible for human hair and casein. The shape of the stress-strain curves for mechanically conditioned wool, human hair, casein, and Vicara fibers thus approaches that of silk in its original state, where no pronounced yield point is observable.

The initial flat portion on the stress-strain curve for the wool yarn after repeated stresses, corresponding to an elongation of approximately 2.8%, is remarkable. Due to the alignment of the individual fibers in the stretching procedure, their crimp, originally present in the yarn structure, was eliminated by mechanical conditioning. The ability of wool fibers to curl again after release of the tension was retained; however, they recurled during the relaxation time of 1 hr., re-forming loose connections with neighboring fibers. These new connections were broken easily and the recovered crimp was removed in the succeeding tensile test at a low, almost undetectable tension, causing the initial flat portion on the stress-strain curve of the mechanically conditioned yarn.

This recurling and mobility of the individual wool fibers in the yarn structure is also revealed by the considerable shrinkage of the wool yarn after cycling in comparison to that of human hair. The recovery behavior of wool yarn and human hair is similar. Their length increased markedly after mechanical conditioning—*i.e.*, to 16.9% and 23.8% of their original length (line 9a, Table I). These length increases were, of course, higher than those calculated from the permanent set values in a single loading * due to the fact that a larger portion of the elongation became "nonrecoverable" in 50 cycles than in a single loading step.

During the relaxation period the wool yarn shrank 6.3% of its initial length, and expanded laterally,

* The permanent set of both fibers (as shown in the upper quadratic graphs of Figure 6) is approximately 38% of their actual elongation at 80% of the elongation at break, to which level the fibers were repeatedly extended (*i.e.*, to actual elongations of 26.6% and 35.5%, respectively). From these values length increases of 10.1% for the wool yarn and 13.5% for hair can be calculated after a single loading step.

while the hair shrank only 2.6% (line 10).* The effect of repeated stresses on the wool yarn is thus to a considerable extent reversible upon relaxation because of the capacity of the individual wool fibers to contract by delayed recovery and to recurl. For the straight hair fibers, on the other hand, delayed recovery is the only source of longitudinal contraction during relaxation. Despite this shrinkage, the length of both fibers remained greater than originally, their length increase being 10.6% and 21.2%, respectively (line 9b). Thus, the final length of the wool yarn was practically identical to that expected (10.1%) from its elongation after a single loading, indicating the complete return of the individual wool fibers to their position before cycling. In contrast to this, the hair after relaxation still remained much longer than calculated from a single loading step (21.2% compared to 13.5%).

The behavior of wool yarn after mechanical conditioning is analogous to that of the "aging" of wool. In a recent systematic investigation of alterations during worsted processing, von Bergen and Wakelin [11] observed that rested wool top expanded laterally and that the energy to uncrimp single fibers (taken out of roving and yarn) increased after resting. They also found that the "maximum load" of the stress-strain curves for rovings was higher after resting. These changes took place rapidly at first, until fairly constant values were reached in approximately 3 weeks. Moist heat, steaming at 185°F (85°C), accelerated this procedure. The "aging" effect was interpreted as a relaxation phenomenon due to the "gradual return of crimp."

The alterations of protein fibers observed after mechanical conditioning reveal the changed morphology (fiber rearrangement and elimination of crimp) as well as the changed fine structure (orientation of crystallites, slippage of long-chain molecules, and formation of new cross-bonds). They are, of course, most pronounced immediately after cycling and diminish during the relaxation period, indicating that morphological and fine-structure changes attained by mechanical conditioning are partly reversible. The relaxation time of 1 hr. used in this study was considered to be sufficient for an approximation of ultimate values. It was probably not long enough to attain equilibrium for the wool yarn in view of the delayed recovery and mobility of the individual wool fibers, both known to be high. Additional progression of relaxation phenomena could therefore take place in the wool yarn in subsequent hours or days after mechanical conditioning.

Effect of Wetting

Yarns of wool, casein, and silk were tested wet with the Instron tensile tester, while the Sookne-Harris tester served for wet tests on single fibers of wool, mohair, human hair, and Vicara. The stress-strain curves obtained are shown in Figure 3. Swelling in water has the effect of increasing the extensibility of the fibers and of weakening them. This is evidenced by lower breaking tenacities, lower yield points, and lower initial moduli. Mohair, silk, and human hair, having relative wet tenacities between 78% and 83%, are less affected by water than wool, casein, and Vicara, whose relative wet tenacities are between 36% and 68%. This behavior is not at all surprising for silk, in view of its high crystallinity and high degree of orientation. Both decrease the swelling of fibers, which occurs mostly in the amorphous part of high polymers. The resistance of the human hair

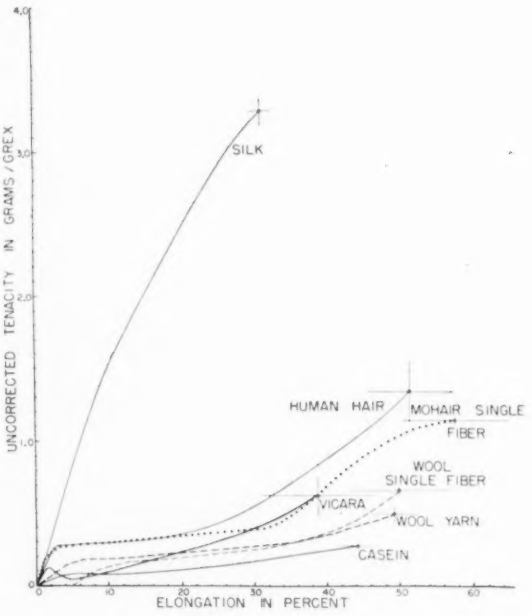

FIG. 3. *Stress-strain curves for wet fibers. Vertical and horizontal lines indicate standard deviations of ultimate values.*

* The difference between the two shrinkages, 3.7%, is similar to the elongation value (2.8%) of the initial flat portion reflecting the rebuilt crimp on the stress-strain curve of the mechanically conditioned yarn.

and mohair specimens to swelling is due partly to their morphology and chemical composition. The ratio between the resistant cuticle cells and the easily affected cortical cells is higher for hair than for wool. Besides this, hair keratin has a higher cystine content (19.0%) than wool keratin (12.2%), and the sulfur cross-bonds of cystine increase the stability of protein molecules. Zahn [12] demonstrated that human hair has a higher "softening point" than wool, 203°F (95°C) compared to 183°F (84°C), when measured by 20% "supercontraction" (shrinkage) in a 1:1 phenol-water mixture. The action of heat is in many cases similar to that of swelling agents, and the higher stability of hair to heat is analogous to its greater resistance to the swelling action of water. The stress-strain curves for the wool yarn and the wool single fiber are similar when wet, except for their initial parts. The flat portion on the curve for the wet single fiber indicates again the crimp (approximately 4.9%).

Recovery Behavior of the Fibers Tested

Behavior of Wool Yarn

The recovery of wool yarn will first be described by actual and then by relative values of the three elongation components.

Actual values of elongation components at standard atmospheric conditions are shown by four curves in Figure 4A. The following observations can be made: Below the yield point the elongation is completely recoverable and the immediate elastic recovery is slightly greater than the delayed recovery. The immediately recoverable portion increases steadily up to the breaking point. A considerable increase of delayed recovery takes place at the yield point. At the breaking point it is much higher than immediate recovery, even slightly exceeding the permanent set. Permanent set starts at the yield point, and increases continuously and rapidly up to the breaking point.

The recovery of the wool yarn tested is thus characterized by a high delayed recovery similar to that of drawn nylon and Vinyon CF-HST, but not observed to this extent in other textile fibers [10]. Most fibers (casein, acetate, silk, viscose) show relatively high permanent set near the breaking point, while others (Fiberglas, Fortisan) are highly elastic, having, however, low extensibility near the point of rupture.

The recovery of the wool yarn was also investigated after mechanical conditioning and when swollen in water. Figure 4B shows the actual values of the three elongation components after repeated stresses. The permanent set starts again at the yield point, which is here fairly close to the breaking point. The permanent set at the breaking point is low compared to that of the original fiber (3.0% *versus* 13.6%). Even this low permanent set is due to the fact that the yarn has been repeatedly extended to only 80% of the elongation at break; therefore, permanent set near the breaking point was not eliminated. Delayed recovery is the predominant elongation component of mechanically conditioned wool yarn. It can be seen that the curves representing immediate and delayed recovery are almost identical to those for the original yarn except for the initial flat section on the curve for delayed recovery after mechanical conditioning, which also appears on the stress-strain curve (the heavy curve in Figure 4B). If the initial flat portion (corresponding to 2.8% elongation) is subtracted from the ultimate value of delayed recovery (16.7%), the remaining value (13.9%) is close to the delayed recovery of the original sample (14.6%).

It is remarkable that the elongation at low strain values (shown by the flat portion) does not recover immediately, as it does for most fibers, but requires some relaxation time.* The relatively high delayed recovery at small, almost undetectable tensions indicates the creeping return of the aligned individual fibers to their former crimped state, and it demonstrates again the mobility of wool fibers in the yarn structure.

Figure 4C shows the actual values of elongation components of the wool yarn after swelling. It is remarkable that only small permanent set appears at high stress and strain values (2.4% at the breaking point). The markedly increased elongation of

* The interpretation of the initial flat portion as delayed recovery may appear questionable from the cycling tests performed, since an initial flat portion is also observable on the second loading curve of mechanically conditioned yarns. Tension is indicated here only after an elongation in excess of approximately 3%. The length of this flat portion in the second loading cycle, however, is identical to that of the first cycle. Besides this, a more or less pronounced slack in the mechanically conditioned yarn is observable in performing cycling tests for small elongations immediately after removal of the tension. The slack disappears progressively during the relaxation time of 5 min. and this manifests the creeping recovery. At elongations higher than 15% a considerable slack remains in the mechanically conditioned yarn after the relaxation time and the length of the flat portion in the second loading curve is now increased. This length corresponds to permanent set.

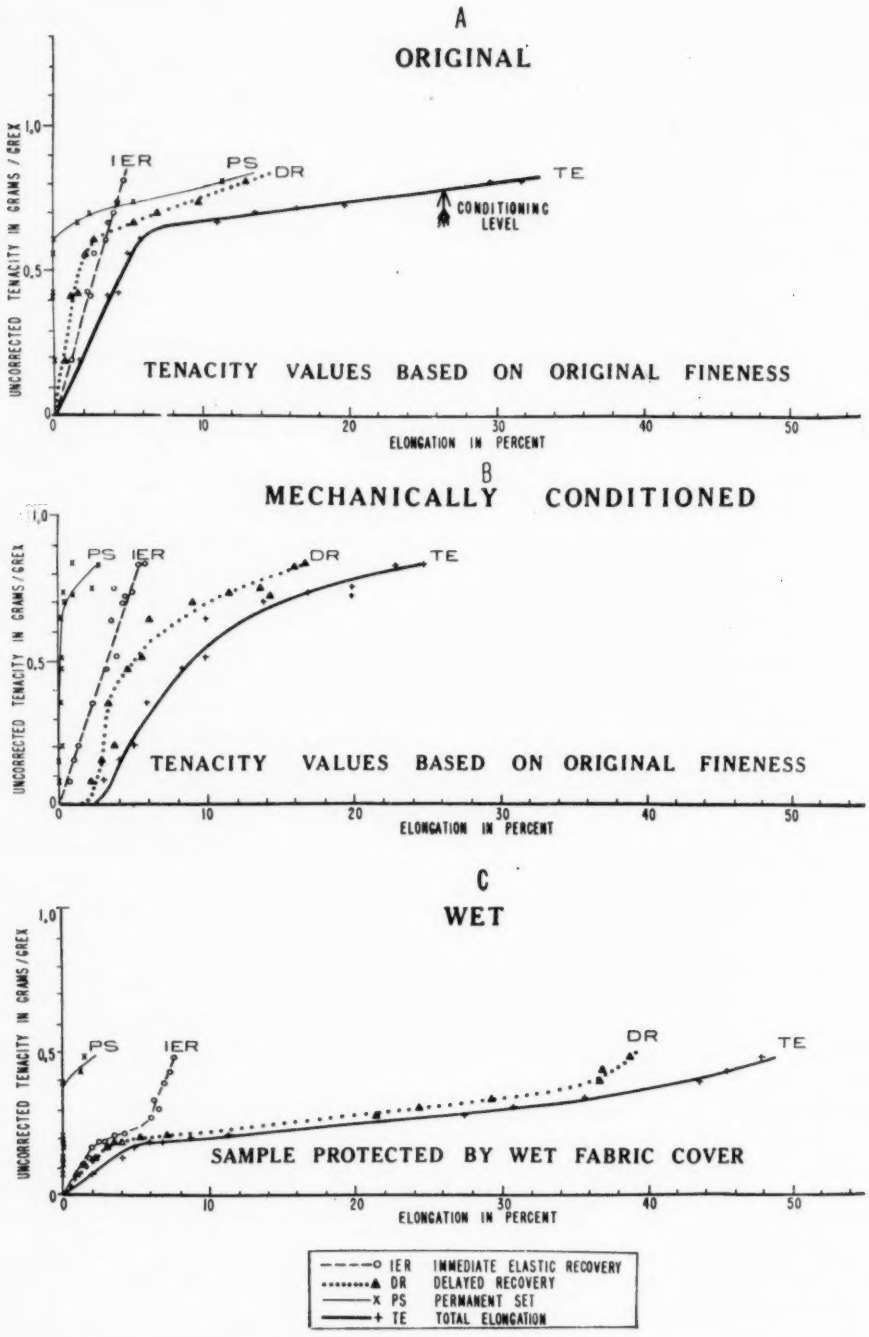

FIG. 4. *Elongation components of wool yarn demonstrated by four curves.*

wet wool (from 33.2% to 49.0%) is thus almost entirely recoverable, confirming the observations of Speakman [9], Harris and Brown [2], Sookne [7], and Maillard, Roehrich, and Fresco [6]. This is typical for natural keratin fibers and is not duplicated (at least to such an extent) by other textile materials. It is also noteworthy that the permanent set of wet wool does not start at the yield point, which is low, corresponding to a tenacity of 0.17 g./grex and an elongation of 5.7%. Permanent set starts at a much higher point (approximately at 0.40 g./grex tenacity and 40% elongation) known as the elastic limit. Differentiation between the yield point and elastic limit is therefore necessary here, although the two coincide in most cases.* Both the immediate and delayed recovery of wet wool increase substantially upon passing the yield point; and the overwhelming portion of the total elongation at the breaking point consists of delayed recovery, having a value of 39.2%, as compared to 14.6% for dry wool.

The recovery behavior of the wool yarn shown from the beginning of the stretching procedure up

* At the yield point a more or less pronounced change in the relationship between stress and strain occurs. Elastic limit designates that point of the stress-strain curve where nonrecoverable elongation (permanent set) starts.

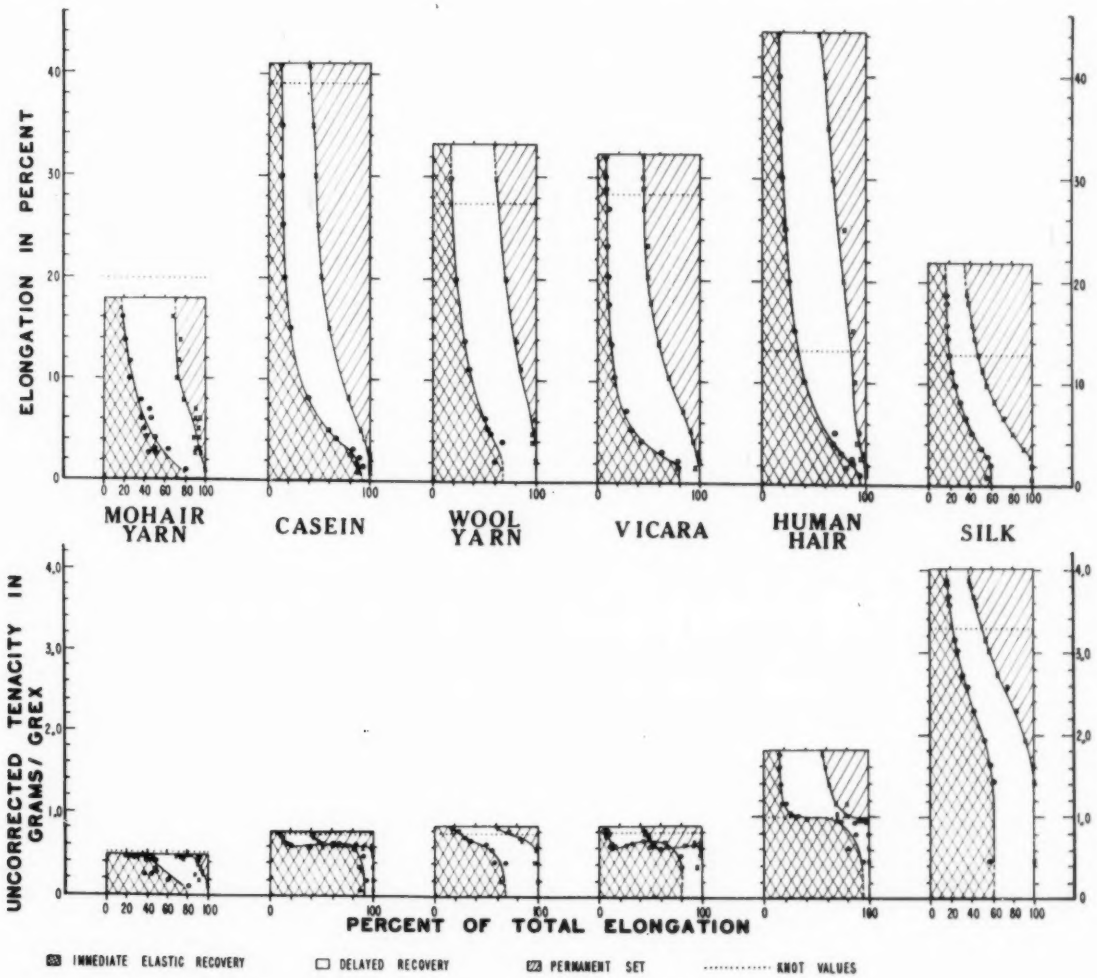

FIG. 5. *Recovery behavior of original fibers.*

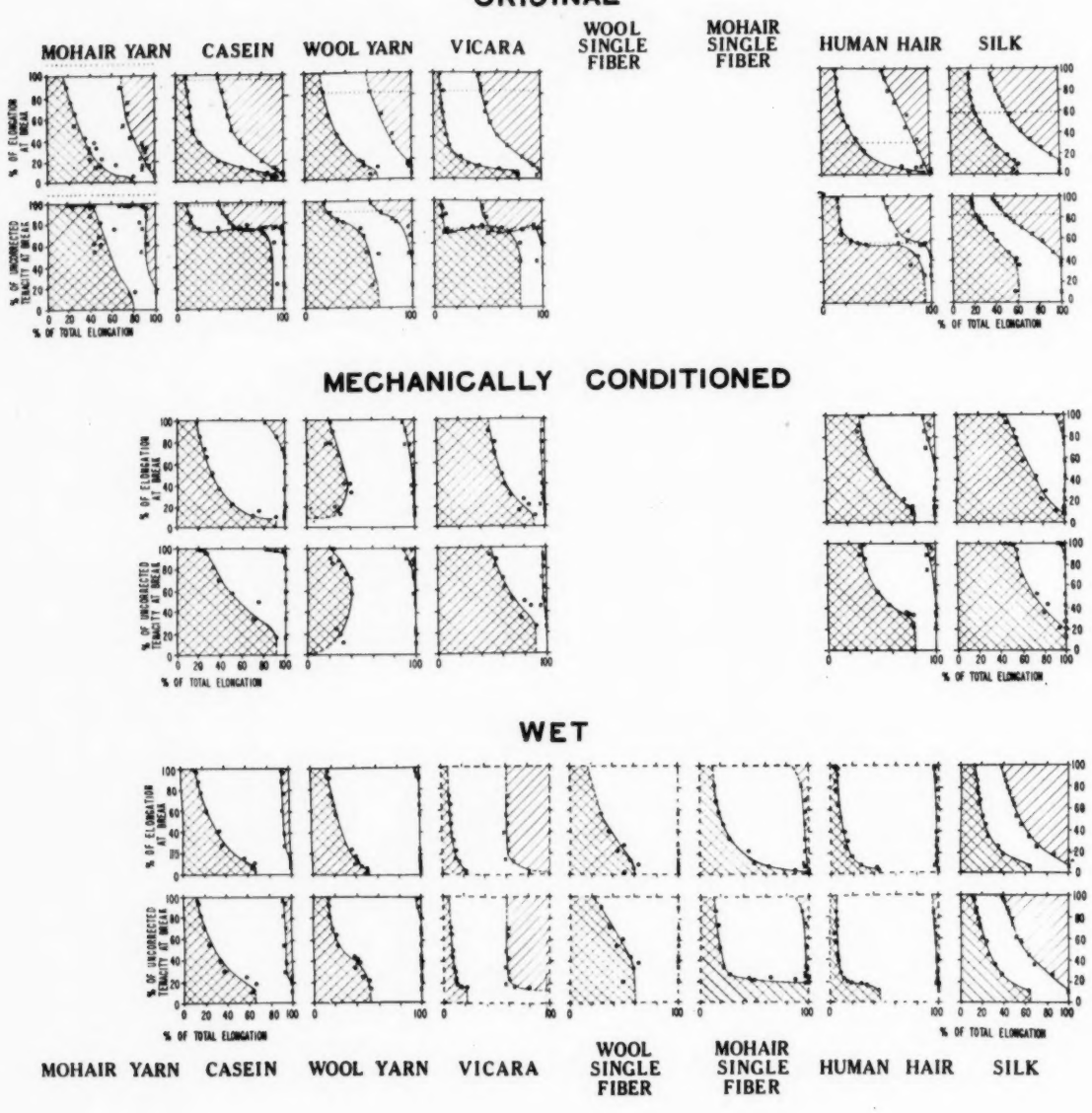

FIG. 6. *Recovery behavior of fibers tested.*

to rupture in Figure 4A can be demonstrated more conveniently by two rectangular graphs (Figure 5) or by two quadratic graphs (Figure 6). Relative values of elongation components are shown here by dividing the graphs into three areas. The following facts are apparent from the graphs: The wool yarn is highly recoverable in its original state, since areas signifying recovery (immediate elastic recovery as well as delayed recovery) occupy the major portion of the graphs. Immediate elastic recovery exceeds delayed recovery at low strain and stress levels. Its relative value decreases rapidly when the elastic limit is passed. Only a small percentage (15%) of the total elongation recovers immediately near the breaking point; a larger percentage (44%) is primary creep, which exceeds even the permanent set (41%). The relative values of delayed recovery do not change substantially during the stretching process.

Recovery of the wool yarn after repeated stresses and when wet is also presented by quadratic graphs in Figure 6. By this demonstration, a convenient comparison under such different test conditions is possible since the considerable differences in ultimate values have been eliminated intentionally. These quadratic graphs show clearly that even the relatively small permanent set of the original wool yarn disappears almost entirely as a result of repeated stresses or wetting. Recovery is, however, immediate only to a small degree.

Behavior of Wool as Compared to Other Protein Fibers

The recovery of protein fibers tested in their original state may be discussed by first considering the rectangles of Figure 5, arranged (as indicated by the height of the graphs in the lower set) in order of increasing tenacity at break. The recovery of natural keratin fibers (wool, mohair, and human hair) appear similar in the rectangles of the upper row despite marked differences in height, representing their extensibility. Nearly identical values of the three elongation components at the same elongation level are shown for these fibers. They all are characterized by relatively small permanent set

TABLE II. RECOVERY BEHAVIOR OF FIBERS TESTED AT THE BREAKING POINT

	Wool single fiber[1]	Wool yarn	Mohair single fiber	Mohair yarn	Human hair single fiber	Casein multi-filament	Vicara single fiber	Silk multi-filament
	Actual Values of Elongation Components (%)							
Original								
Immediate elastic recovery		5.0		3.0	6.2	4.1	2.3	3.4
Delayed recovery		14.6		9.5	18.6	11.9	11.6	4.5
Permanent set		13.6		5.3	19.6	25.0	18.4	13.9
Mechanically Conditioned[2]								
Immediate elastic recovery		5.6			6.0	2.6	4.8	3.2
Delayed recovery		16.7			11.2	8.4	5.0	3.3
Permanent set		3.0			1.7	2.7	0.3	0.5
Wet								
Immediate elastic recovery	7.2*	7.4	7.0*		3.6*	6.2	1.9*	4.0
Delayed recovery	37.8*	39.2	42.0*		45.6*	34.9	21.0*	8.4
Permanent set	0*	2.4	8.5*		2.1*	3.1	15.9*	20.7
	Relative Values of Elongation Components (%)							
Original								
Immediate elastic recovery		15		17	14	10	7	16
Delayed recovery		44		53	42	29	36	20
Permanent set		41		30	44	61	57	64
Mechanically Conditioned[2]								
Immediate elastic recovery		22			32	18	48	46
Delayed recovery		66			59	62	49	47
Permanent set		12			9	20	3	7
Wet								
Immediate elastic recovery	16*	15	12*		7*	14	5*	12
Delayed recovery	84*	80	73*		89*	79	54*	25
Permanent set	0*	5	15*		4*	7	41*	63

[1] Without crimp.
[2] Correlated to the new length after mechanical conditioning.
* Values obtained using the Sookne-Harris tester.

and high recovery even at the breaking point, the major part of recovery being delayed. The recovery of casein and Vicara differs slightly from these fibers in that the nonrecoverable portion of the elongation is increased and recovery is lower at the breaking point. The behavior of silk is markedly different, however, It has a high permanent set (especially near the breaking point), and significantly diminished delayed recovery. The immediate elastic recovery of silk is nearly equal to that of the other protein fibers when compared at the same elongation level.

The recovery behavior of the fibers tested originally, after mechanical conditioning, and when wet can be compared best by the three sets of quadratic graphs * in Figure 6 (arranged in the order of increasing tenacity in the original state). Numerical data of the corresponding actual and relative values of elongation components at the breaking point are listed in Table II.*

The quadrates representing the recovery of the mechanically conditioned fibers demonstrate that permanent set is almost entirely eliminated from all of the five fibers tested after repeated stresses. This behavior is similar to that of other textile fibers, and causes their markedly diminished extensibility after mechanical conditioning. There are differences, however, in the recovery, with that of Vicara and silk being to a great extent immediate, and that of casein, wool, and human hair being predominantly delayed, especially near the breaking point.

The quadrates representing the recovery behavior of wet fibers show the following facts: casein, wool, mohair, and human hair have similar recovery characteristics in that permanent set disappears almost entirely and delayed recovery is predominant. The wool single fibers are entirely elastic, and no permanent set is observable despite the limitations of the Sookne-Harris tester, which necessitated a lower jaw speed to be used in these tests favoring plastic flow. Only a small permanent set is observable on wool yarn near the breaking point, and its origin is most likely fiber slippage at high tension. The recovery of Vicara is interesting since the elongation components have almost the same relative values from the beginning of stress and strain up to the breaking point. A relatively high percentage of the elongation is nonrecoverable, however, which is in contrast to the behavior of casein and the keratin fibers. The areas of the three elongation components in the quadrates for silk in its original state and when wet are not very different from each other. Relative values of recovery thus remain almost unchanged by swelling, despite marked differences in the yield point, in the entire stress-strain relationship, and in the ultimate values.

An increased recovery is characteristic for most protein fibers when swollen in water. It is very pronounced for natural keratins and it can also be observed in the regenerated protein fibers, casein and Vicara. Silk, however, does not have this behavior.

* The results of recovery tests using the Sookne-Harris tester are shown in Figure 6 by quadrates with a dashed frame to differentiate them from the more representative tests made on the Instron. The Sookne-Harris values in Tables I and II are differentiated from the rest by asterisks

Summary

Knowledge of the tensile behavior of the protein fibers—wool, mohair, hair, casein, Vicara, and silk—has been extended to include quantitative data on their elastic recovery. Needed information has also been obtained by investigating the influence of repeated stresses and of swelling. It has been shown that the recovery of wool in its original state is exceptional, that after mechanical conditioning it is similar to that of other fibers, and that it is unique when wet. The investigation of a mechanically conditioned wool yarn revealed that although the crimp of the individual wool fibers is removed by stretching, it is rebuilt spontaneously during the relaxation period. The restoration of crimp manifests the ability of individual wool fibers to recurl and to change their positions in relation to each other within the yarn structure after the strain or stress has been released. This mobility of wool fibers, the high elastic recovery, and the improvement in recovery when wet are properties not present (at least to such an extent) in other textile fibers. These characteristics are basically responsible for the resilience, crease-retention, wrinkle-resistance, excellent dimensional stability, hand, and liveliness of woolen fabrics.

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Correction

In the article "The Identification of Synthetic Fibers by Their Refractive Indices and Birefringence," by A. N. J. Heyn, which appeared in the April, 1953, issue of TEXTILE RESEARCH JOURNAL, the second sentence of the caption for Figure 2 (on p. 248) should read: "*Plane of light vibration is along vertical line in* 1 *and* 2 (*refractive index of vertical fiber 1.700 and of horizontal fiber 1.532*), *and along horizontal line in* 3 *and* 4 (*refractive index of vertical fiber 1.532 and of horizontal fiber 1.700*)."

A Study of Soiling and Soil Retention in Textile Fibers*

The Effect of Yarn and Fabric Structure in Soil Retention†

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IN previous papers of this series [3, 4, 5, 10, 11] the nature of the bond between soil and fiber surfaces was studied using the chopped-fiber technique, which eliminated the complicating factors of yarn and fabric construction.

As stated in previous publications in this series, macro-occlusion, or entrapment of soil particles in the interfiber and interyarn spaces, is a factor of importance in soil retention. The objective of the present investigation was to determine the relative importance of macro-occlusion due to yarn and fabric construction on the soil retention of fabrics.

The physical factors affecting the reflectance of soil-fabric systems are also given detailed consideration.

Theoretical

The theory of the optical characteristics of turbid media has been contributed to by many authors, including Kubelka and Munk [13, 14], Duntley [7], Gurevic [9], Amy [1], and others. These studies, however, do not relate the optical factors of the systems in question to the amount or concentration of light-absorbing material. This has been attempted by Derby [6], Nolan [16], Foote [8], and Preston and Tsien [17] in the case of dyed fabrics and papers, but not in the case of pigmented systems such as are exemplified by soiled fabrics.

It has been shown by Utermohlen and Ryan [18], Lambert and Sanders [15], and others that the equations derived from purely optical considerations cannot be related directly to the total amount of soil or pigment in a soiled fabric. The physical reasons for this failure apparently have not been discussed in the literature, and it is therefore a matter of some interest to examine these and to attempt to determine whether conditions can be defined and techniques developed such that an accurate correlation of soil content with reflectance can be obtained.

If we consider the Kubelka-Munk equation as applied to fabrics containing various amounts of soil, then

$$\frac{K}{S} = \frac{(1 - R)^2}{2R}, \qquad (1)$$

where R = reflectance, K = light-absorption coefficient, and S = light-scattering coefficient.

In order to determine soil concentrations by use of this equation, the assumption is made that K is proportional to the amount of light-absorbing material present [13]. For this assumption to be valid, three conditions must exist—namely, (*1*) the distribution of soil particles in the fabric must be uniform, or at least identical in the fabrics tested; (*2*) the particles must be dimensionally isotropic or if anisotropic they must have random orientation; and (*3*) the specific absorbance of the soil must be known or constant.

Recognizing the requirements of the equation, an analysis of the conditions and the factors which affect them can be made.

In fabrics, it is practically impossible to achieve uniform distribution of the soil. Two limiting types of nonuniform distribution can be distinguished. The first type of nonuniform soil distribution in soiled fabric is *planar nonuniformity*. This is the streaking, spotting, and patchiness of applied soil on the fabric which causes reflectance values to vary from one observation site to another over the surface of a piece of fabric. If the reflectance values obtained at a series of points are plotted against the distances along the fabric surface, this type of nonuniformity is made apparent (Figure 1).

* A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

† Presented before the Fall Meeting of The Fiber Society at Princeton, N. J., Sept. 10, 1952.

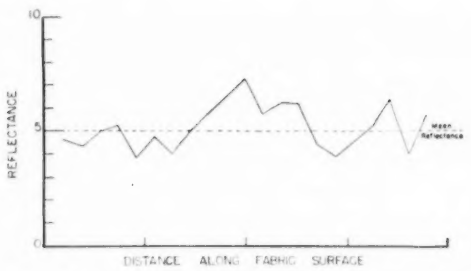

FIG. 1. *Schematic graph showing planar nonuniformity of soil distribution in fabric.*

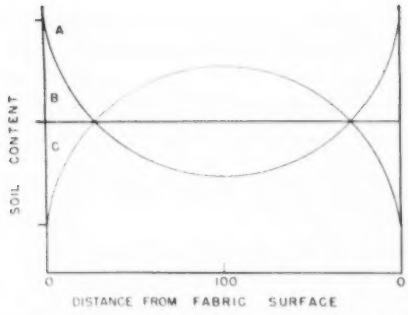

FIG. 2. *Schematic graph showing orthogonal nonuniformity of soil distribution in fabric.*

In practice, this type of nonuniformity of soiling is averaged to give reproducible results, either by taking a large number of reflectance readings or by using a reflectometer, which measures the reflectance of a large area of the soiled fabric surface. For wash tests, particularly multicycle laundering, these procedures for averaging reflectance carry the inherent possibility of sampling error arising from changes in the relative proportions of light and dark area zones, or spots, in an unpredictable manner.

The second type of nonuniformity of soil distribution is *vertical* or *orthogonal nonuniformity*, which does not appear to have been reported in the literature concerned with fabric soiling. A schematic representation of some of the types of orthogonal soil distribution which may occur in soiled fabrics is shown in Figure 2.

If we consider a fabric of an arbitrary thickness of 200 units, then the distributions of soil content at various plane levels parallel to the fabric surface may be plotted to obtain the curves shown. It is readily seen that for identical total soil concentrations there may be obtained three soiled-fabric reflectance values, $R_C > R_B > R_A$, due to the exponential penetration curve of the test light beam. This type of nonuniformity of soil distribution is particularly apt to vary during soiled-fabric laundering tests, as consideration of the diffusion process makes plain.

It should be emphasized that each of the simple types of nonuniformity described above is a limiting case, and that in real systems both probably occur simultaneously. Microscopic examination of soiled fabrics confirm this.

Orientation is of importance only in the case of particles which are highly anisotropic geometrically, such as needles, rods, or platelets. It has been shown for dispersions in fluid media that thermal motion or turbulence randomizes the particle positions to produce the case of zero orientation relative to the test light beam. In the case of fabrics, this will not be true, however, and it seems likely that particle orientation will be influenced by the geometry of the interyarn and interfiber spaces which, though complex, is far from being isotropic.

The specific absorbance, which defines the third condition for validity of the Kubelka-Munk equation, may be most easily understood by considering an ideal case. Let us assume that the soil particles are a perfectly monodisperse group of spheres with completely uniform distribution and an absorption coefficient of unity (perfect black bodies). Their specific absorbance will then be equal to the area of a section through the center of each sphere multiplied by the factor N, the number of particles per gram. In a fabric, as has been pointed out by Preston and Tsien [17], the reflection from the fiber interfaces gives rise to a general diffusion of the incident light rays. This makes it necessary to deal with the case of spherical absorbance in a pigment particle.

We may now consider a real particle, in such a system, exposed to and absorbing light from all directions. Suppose that such a particle is encased in the smallest sphere which can contain it. Take a plane of projection of the particle which is tangent to the surface of the containing sphere. The summation of the rectilinear projections at n points on the surface of the sphere divided by n is

$$A = \frac{\sum_{1}^{n} a}{n}, \qquad (2)$$

where A = average projection area of the particle, a = area of each projection, and n = number of projections.

For a real soil containing N particles per gram the average projection area per particle, α, is

$$\alpha = \frac{\sum_{1}^{N} A}{N}. \quad (3)$$

The average absorbance per particle, x, is then

$$x = k\alpha, \quad (4)$$

where k is the coefficient of light absorbance of the pigment. It is assumed that the value of k for the particle does not differ appreciably from the value for the massive form.

The specific absorbance, X, for a real soil of N particles per gram may then be defined as

$$X = kN\alpha. \quad (5)$$

Then for the Kubelka-Munk factor, K (equation (1)),

$$K = M_p X, \quad (6)$$

where M_p = mass of pigment in grams. By substituting in the Kubelka-Munk equation,

$$\frac{M_p X}{S} = \frac{(1 - R)^2}{2R}, \quad (7)$$

or

$$M_p = \frac{S(1 - R)^2}{2RX}, \quad (8)$$

provided the conditions of uniform distribution and random orientation of the soil are satisfied.

This will very seldom be the case in soil-fabric systems. It is possible, however, to eliminate the factors of fabric and yarn structure, nonuniformity of soil distribution, and orientation by the simple expedient of chopping the fabric, slurrying the chopped fiber, and depositing it as a fiber pad. It is then possible to solve equation (6) for the specific absorbance in the case of a system containing a known mass of pigment, or to solve equation (8) if the specific absorbance of a pigment has been determined.

For most cases in the study of detergency, it is not necessary to compute M_p or X. If the specific absorbance is constant, or approximately so, it is evident from equation (6) that K/S is directly proportional to M_p and may be used as an index for this quantity. If we are interested in the percentage of soil removed from a soiled fabric by various treatments, then Bacon and Smith's [2] equation may be used:

$$\frac{(K/S)_{SF} - (K/S)_{WF}}{(K/S)_{SF} - (K/S)_O} \times 100 = \text{percent soil removal}, \quad (9)$$

where $(K/S)_{SF}$ = the K/S value for the soiled fabric, $(K/S)_{WF}$ = the K/S value for the soiled and washed fabric, and $(K/S)_O$ = the K/S value for the unsoiled fabric.

It might be asked at this point how we are to detect or evaluate changes of the specific absorbance, which is admittedly a complex variable (see equation (5)), and one which can undergo large changes during testing procedures. For detergency studies this may be done as follows. The K/S value is determined for the original soiled swatches using the fiber-pad K/S value, and then K/S values are obtained similarly for the washed swatches, the redeposit swatches, and for the bath. In order to compute the K/S value for the bath liquor, a procedure such as that given by Vaughan and Smith [19] may be employed. Then

$$(K/S)_T = (K/S)_{WF} + (K/S)_{RS} + (K/S)_B, \quad (10)$$

where $(K/S)_T$ = total K/S value after washing, $(K/S)_{WF} = K/S$ value for the soiled and washed swatches, $(K/S)_{RS} = K/S$ value for the redeposit swatches, and $(K/S)_B = K/S$ value for the bath liquor.

$$\left[\frac{(K/S)_T}{(K/S)_{SF}} - 1\right] \times 100 = \text{percent change in specific absorbance}, \quad (11)$$

where $(K/S)_{SF}$ = K/S value for the original soiled swatch.

The specific absorbance thus obtained is that for the entire system, and may vary between the component parts, but for small changes this will not be important and obvious procedures will permit close approximation for any single component. Anomalous cases where large deviations occur are easily recognized.

In the work which is to be discussed regarding the effect of yarn and fabric structure, three quantities of interest are considered—namely, (*1*) soil content of various systems, (*2*) orthogonal nonuniformity of different systems, and (*3*) percentage increase of soil retention due to macro-occlusion (macro-occlusion index).

As has been shown above, the K/S value is an index to the soil content of a given system. Judd [12] published a complete table of these values from $100\,R = 0.1$ to $100\,R = 100.0$, eliminating the necessity of computation.

The index of orthogonal nonuniformity is given by the following equation:

$$\frac{(K/S)_{CF}}{(K/S)_{Fab}} = I \qquad (12)$$

where I = index of orthogonal nonuniformity, $(K/S)_{CF} = K/S$ value for the chopped fiber pad, and $(K/S)_{Fab} = K/S$ value for the original fabric.

If I is greater than 1.1, type C distribution is present (see Figure 2). If it is between 0.9 and 1.1, type B, or uniform distribution is the case. For values less than 0.9, type A distribution occurs.

The percentage of soil held by macro-occlusion is defined by the equation

$$\left[\frac{(K/S)_{CF}}{(K/S)_F} - 1\right] \times 100 = \text{percent macro-occluded soil,} \qquad (13)$$

where $(K/S)_{CF} = K/S$ value for the fabric which has been soiled, classified, and chopped, and $(K/S)_F = K/S$ value for chopped, soiled, and classified fibers. The amount of surface-bound soil is considered as 100%.

Experimental

General Methods

In this investigation commercial fabrics, or chopped fibers prepared from them, were used. To prepare chopped fibers, the fabrics were cut into strips which were fed into a standard-size Wiley mill, using a 20-mesh screen to give a fiber length range of 0.1 to 1 mm. The chopped fiber was scoured for 30 min. in a 0.5% aqueous soap solution to remove oils and finishes, and then rinsed by decantations and filtration. After eight to ten decantations with water, the soap and finish were removed. The original fabrics were scoured, using a similar procedure.

The standard carbon black dispersion was prepared from Germantown Lampblack,* using a 0.15% Daxad-23 water solution as the dispersion medium. A dispersion containing 20 g./liter of carbon black was prepared using a colloid mill, followed by centrifuging the dispersion for 20 min. at 1500 r.p.m. in a model SB-2 International centrifuge using a 6-in. head. The concentration of the carbon black in the resulting dispersion was found to be 10 g./liter, and presumably a smaller and more uniform particle-size distribution resulted. Chopped fibers were soiled by the techniques previously described [2, 3, 4, 9, 10], whereas fabrics were soiled by a filtration process. In the latter process the fabrics were cut into disks which fitted a 5¾-in. diameter sintered nickel filter funnel. The carbon black dispersion was filtered through the fabric pad three times under light suction; the pad was then reversed, and the operation was repeated three times.

Both primary and secondary soil depositions were investigated. In primary deposition studies the soiled fabric was transferred immediately to a beaker of tap water and given successive rinsings until no more carbon black could be observed in the rinse water. In secondary deposition studies the soiled fabric was air-dried at a temperature of 105°C for 2 hrs. and then rinsed until no further loss of carbon black could be observed in the rinse water.

Studies of primary and secondary deposition of soil on chopped fibers were carried out using techniques described in previous publications [3, 4, 5, 10, 11].

Effect of Fabric Structure on the Retention of Carbon Black Soil by Cotton Fabrics

The results obtained for the primary deposition of carbon black soil on various cotton fabrics and on chopped cotton fibers are summarized in Table I.

The apparent retention of soil is given in the columns under "Soiled fabric." The true soil index is shown in the columns under "Chopped soiled fabric," and the nonuniformity index (NU ratio) increases with the complexity and weight of the fabric structure, as would be expected. The effect of macro-occlusion resulting from primary soil deposition also increases as the complexity and weight of fabric structure increases.

Secondary soil deposition was found to be more complex (Table II). The total soil retention was found to be high, the NU ratio relatively high, and, as with primary deposition, a type C distribution occurs. The percent increase in soil pickup due to

* The mention of trade products in this paper does not imply their endorsement by the Department of Agriculture over similar products not mentioned. Differences shown in the results obtained with trade products do not prove or imply superiority of any one over any other in the applications for which these products are normally intended.

macro-occlusion is large, indicating an agglomerative build-up of soil within the fabric structure.

Effect of Fabric Structure on the Retention of Carbon Black Soil by Fabrics Constructed of Fibers Other than Cotton

Since macro-occlusion is found to be a major factor in the retention of soil by cotton fabrics, it was of interest to determine whether this was true for fabrics constructed of fibers other than cotton. Linen, nylon, silk, and wool fabrics were chosen as a representative group of commercially important fibers.

The results obtained for the primary deposition of carbon black are summarized in Table III. Nylon shows the lowest primary deposition, which is probably due to the smoothness and low wettability of nylon fiber. It is interesting to note that heavy complex yarns, such as those used in linen and wool fabrics, exhibit high increases in soil retention over that of the fibers. Type *C* nonuniformity is found for both primary and secondary soil deposition for all of the fabrics.

The extremely large macro-occlusion index for secondary deposition on nylon is most probably due to agglomerative build-up within the fabric structure (Table IV). The fabrics made from other fibers

TABLE I. EFFECT OF COMPLEXITY OF STRUCTURE ON PRIMARY DEPOSITION OF CARBON BLACK ON COTTON FABRICS

Material	Soiled fabric		Chopped soiled fabric		Soiled chopped fibers		*NU* ratio	Increase of soil pickup due to macro-occlusion (%)
	$R\%$*	K/S	$R\%$	K/S	$R\%$	K/S		
Print cloth, 56 × 44	61	0.125	55	0.184	62	0.117	1.47	58
Print cloth, 80 × 80	54	0.196	41	0.425	60	0.133	2.17	219
Cotton flannel, 4 oz.	50	0.250	25	1.125	62	0.117	4.50	866

* $R\%$ = photovolt reflectometer reading.

TABLE II. EFFECT OF COMPLEXITY OF STRUCTURE ON SECONDARY DEPOSITION OF CARBON BLACK ON COTTON FABRICS

Material	Soiled fabric		Chopped soiled fabric		Soiled chopped fibers		*NU* ratio	Increase of soil pickup due to macro-occlusion (%)
	$R\%$	K/S	$R\%$	K/S	$R\%$	K/S		
Print cloth, 56 × 44	22	1.38	12	3.23	46	0.32	2.34	920
Print cloth, 80 × 80	33	0.68	13	2.91	48	0.28	4.28	930
Cotton flannel, 4 oz.	20	1.60	10	4.05	46	0.32	2.53	1180

TABLE III. EFFECT OF COMPLEXITY OF STRUCTURE ON PRIMARY DEPOSITION OF CARBON BLACK ON FABRICS PREPARED FROM VARIOUS TYPES OF FIBERS

Material	Soiled fabric		Chopped soiled fabric		Soiled chopped fibers		*NU* ratio	Increase of soil pickup due to macro-occlusion (%)
	$R\%$	K/S	$R\%$	K/S	$R\%$	K/S		
Linen, 47 × 33 (6 oz.)	36	0.569	27	0.987	74	0.046	1.73	2045
Nylon, 138 × 89 (2 oz.)	55	0.184	47	0.299	77	0.034	1.73	780
Silk, 167 × 68 (2½ oz.)	34	0.641	26	1.053	59	0.143	1.64	640
Wool, 55 × 43 (6 oz.)	44	0.356	39	0.477	66	0.088	1.34	442

TABLE IV. EFFECT OF COMPLEXITY OF STRUCTURE ON SECONDARY DEPOSITION OF CARBON BLACK ON FABRICS PREPARED FROM VARIOUS TYPES OF FIBERS

Material	Soiled fabric		Chopped soiled fabric		Soiled chopped fibers		*NU* ratio	Increase of soil pickup due to macro-occlusion (%)
	$R\%$	K/S	$R\%$	K/S	$R\%$	K/S		
Linen, 47 × 33 (6 oz.)	31	0.768	19	1.727	44	0.356	2.25	385
Nylon, 138 × 89 (2 oz.)	32	0.722	15	2.41	71	0.059	3.34	4000
Silk, 167 × 68 (2½ oz.)	20	1.600	9	4.60	18	1.868	2.87	146
Wool, 55 × 43 (6 oz.)	13	2.91	11	3.60	26	1.053	1.24	242

show a similar phenomenon, but to a lesser degree, due to relatively high secondary deposition on the free fiber surface.

Discussion

In previous papers of this series [2, 3, 4, 9, 10] soil macro-occlusion in soiled fabric structures, or entrapment of soil in the interfiber and interyarn spaces, was found to be eliminated by use of the chopped-fiber technique.

The importance of macro-occlusion is shown in Tables I, II, III, and IV. Macro-occlusion must, then, be considered a major factor in soil retention for both primary and secondary soil deposition. Natural soiling by smokes, dusts, or liquid-borne soils such as mud splashes, etc., very probably leads to the entrapment of soil in the interyarn and interfiber spaces of the fabrics. This type of soil retention is probably operative during the early stages of laundering, and may also be responsible for the tenacious retention of redeposited soil in fabrics.

It seems obvious that high concentrations of soil in the wash liquors during all stages of laundering should be avoided. Diffusion of a heavily soiled bath liquor into the fabric structure will produce interfiber concentrations of soil which can be reduced to negligible levels only by an uneconomically large number of rinsings. The difficulty of detaching dried or grease-bound soil from interior fiber surfaces further complicates the soil removal problem, as may be seen from the results obtained on secondary deposition.

Conclusions

1. Necessary conditions for the application of the Kubelka-Munk equation to fabric-soil systems for the determination of soil content from reflectance measurements have been given—namely, (*a*) uniformity of particle distribution in the fabric, (*b*) random orientation of the soil particles, and (*c*) the specific absorbance of the soil must be either known or constant.

2. The two simple limiting types of nonuniformity of distribution of soil or pigment in fabrics were discussed—namely, planar nonuniformity and orthogonal nonuniformity.

3. The specific absorbance of a dispersed soil is the summation of the optical absorbances of the individual soil particles. The absorbance of the soil particle in turn is derived from the physical factors of size, shape, and light-absorbance coefficient.

4. Direct application of the Kubelka-Munk equation, or immediately derivative equations, to soil-fabric systems fails because of the physical factors which have been discussed. In such systems the conditions of validity described in (1) are only seldom fulfilled. Methods are outlined by which these conditions can be satisfied.

5. The phenomenon of macro-occlusion, or interfiber and interyarn entrapment, of soil particles in fabric structures has been studied for several types of fibers and fabrics and found to be a major factor in soil retention in all cases, both for primary and secondary soil deposition.

6. In general, as the weight and complexity of fabric structures increase, the number of macro-occluded soil particles increases.

7. Orthogonal nonuniformity occurred in all the fabrics tested. Type *C* distribution appeared to be the general rule.

8. It is suggested that soil particle macro-occlusion in soiled fabric structures is largely responsible for the difficulty experienced in removing soil during laundering and in obtaining consistent and precise detergency data.

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A Two-Dimensional Load-Extension Tester for Woven Fabrics

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Abstract

A two-dimensional load-extension tester for woven fabrics has been constructed. The apparatus imposes simultaneous extensions on a sample in two mutually perpendicular directions. A strain-sensing element measures the internal strain developed in the homogeneously strained region as a function of the dynamically varying load. Preliminary results indicate important differences in behavior of fabrics under one-dimensional tests and under two-dimensional tests. The latter are believed to simulate better the conditions that a fabric sustains in actual use.

In laboratory determinations of the load-extension properties of fabrics, the existing techniques consist mainly of the application of load in one direction and the measurement of strain in that direction [1]. In actual use, however, a fabric is ordinarily subject to forces in several directions simultaneously. As a result there is developed a "cross-straining" that cannot be studied in a one-dimensional test. In order to provide a more fruitful basis for predicting the behavior of a fabric in field use from the behavior in laboratory tests, a test apparatus has been constructed to permit the measurement of cross-straining when stretching forces are applied simultaneously in more than one direction. Multidirectional test devices have been described by Ariano [3], who developed a static-load two-dimensional tester for rubber films; Anderson [2] and Boonstra [4], who used a pressure-cylinder apparatus suitable for impermeable sheets; and Treloar [6], who built an apparatus for imposing four-directional planar strains in rubber, but without provision for measuring loads. However, none of these devices is suitable for studying dynamic load-extension properties of fabrics permeable to air. Consequently, an apparatus has been designed to extend a fabric in two mutually perpendicular directions at the same time, with provision to record continuously the force developed in one direction as a function of the strain imposed in that direction. To get more complete information on a given ma-

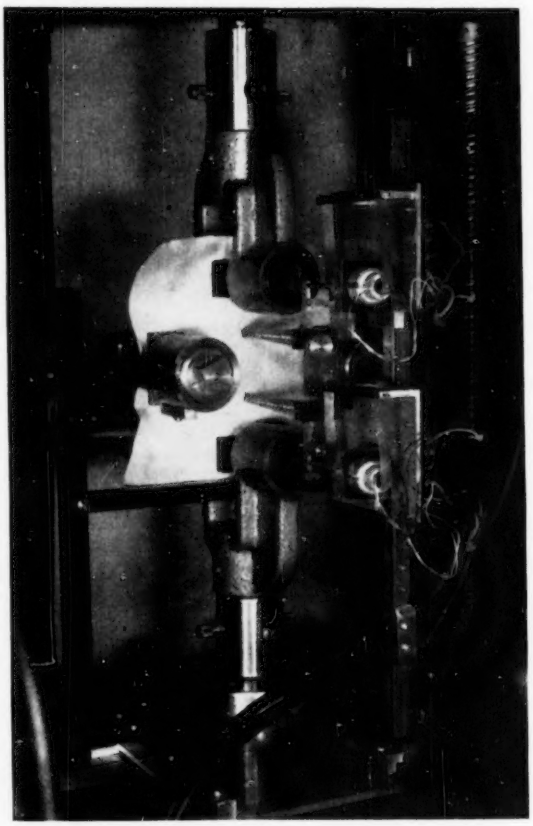

FIG. 1. *Two-dimensional load-extension tester in place on Instron tensile tester.*

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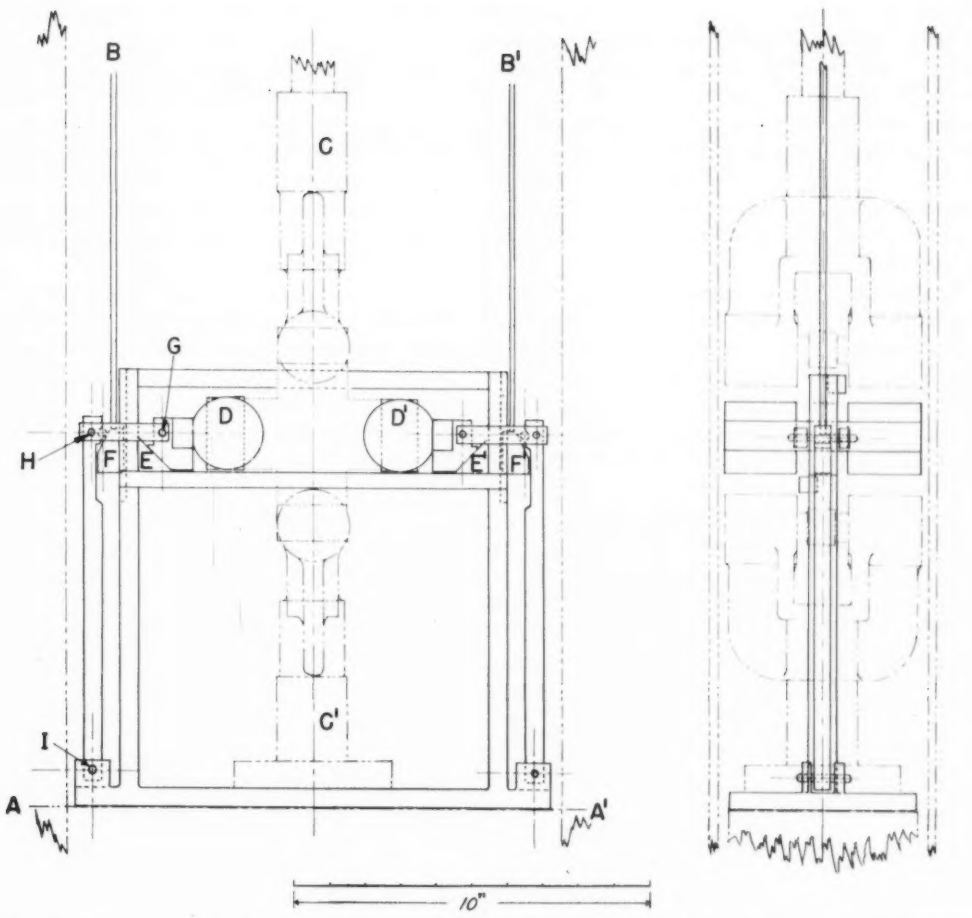

FIG. 2. *Two-dimensional load-extension tester. A–A'—Top of tester crosshead. B, B'—Rods connected to the tester frame. C—Upper jaw of tester. C'—Lower jaw of tester. D, D'—Horizontal jaws. E, E'—1 × 1 wedges. F, F'—1 × 2 wedges. G, H, I—Pivot points.*

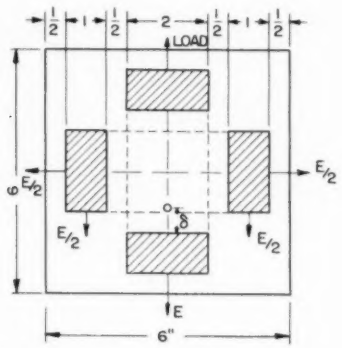

FIG. 3. *Fabric sample as held in place by testing jaws.*

terial, additional tests are made on samples rotated through 90° or some other angle. A strain-sensing device has been constructed for use in conjunction with this apparatus to allow measurement of the strain within the homogeneously cross-strained central region of the sample.

Two-Dimensional Extension Element

The extension element is in the form of an apparatus to be installed in a standard Instron tensile-testing machine. The apparatus consists of an arrangement of clamps and wedges to allow simultaneous extension of a fabric sample in two mutually per-

pendicular directions. Figure 1 is a photograph of the two-dimensional force-extension apparatus in place in the testing space of the Instron machine. (In the photograph is shown also the strain-sensing element, to be described later.) Figure 2 is a sketch showing some constructional details of the extension element. The square test sample of fabric is held by four self-aligning jaws with built-in nylon-faced constant-pressure buttons, according to the pattern shown in Figure 3.

When the crosshead of the tensile-testing machine is displaced, the bottom jaw moves with it at a predetermined constant rate. The top jaw remains fixed and transmits the vertical force on the fabric to the Instron force-sensing element. The two side jaws move apart simultaneously at a rate determined by the speed of the crosshead and by the angle of the wedges chosen for the experiment. In the preliminary experiments to be described in this paper, the angles are taken so as to maintain equal rate of strain in both the horizontal and the vertical directions. In order to get a stress-strain pattern symmetrical about the center of the test sample, the side jaws were made to move upward with respect to the lower jaw at a rate of motion equal to half that of the lower jaw.

Strain-Sensing Element

Because the strain pattern is not uniform throughout the sample (see Figure 3), the *internal strain—i.e.*, the strain within the homogeneously stretched central region—cannot be assumed to be equal to the *external strain—i.e.*, the strain averaged over the entire sample length. Consequently, it is necessary to measure the internal strain directly. The element adopted for this purpose consists of two separate deflection gages mounted on a support fixed to the Instron crosshead, as shown in the right foreground of Figure 1. A schematic drawing of the device is presented in Figure 4. Each deflection gage consists of a balanced bell crank and a linear variable differential transformer (*LVDT*), whose core is displaced by motion of one end of the bell crank. The other end of the bell crank carries a needle whose tip is inserted in the fabric and thereby serves as the deflection-measuring point. A vertical displacement of the needle point inserted in the fabric sample pro-

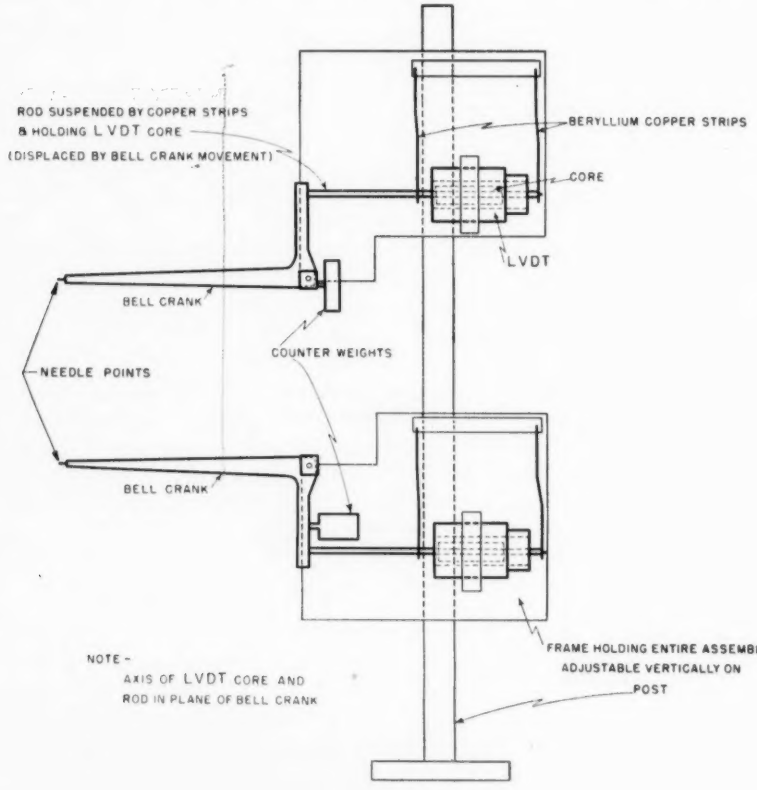

FIG. 4. *Strain-sensing element for determining internal strain.*

duces a proportional signal from the *LVDT*. By electrically subtracting the output of one *LVDT* from that of the other, a signal proportional to the relative displacement of the two test points is obtained. This signal, a measure of the internal strain, is recorded against external strain on a two-pen automatic recorder simultaneously with the signal from the force-sensing element of the Instron machine. The recording circuit which has been used here is essentially that described by Reichardt, Schaevitz, and Dillon [5].

It is possible to dispense with one of the deflection gages, and the concomitant electrical subtraction, if it can be established that the sample is strained symmetrically about its center throughout the cross-strained area. This has indeed been found to be the case with fabrics of ordinary uniformity, and the range of strain measurable with a given strain-sensing system can thereby be increased. Moreover, the sample has been found to be strained uniformly within a 0.95-in. square region about the center.

Preliminary Results

As an example of the type of information available with the two-dimensional tester, Figure 5 shows load-extension curves to break for a plain-weave cotton fabric (weight, 1.95 oz./sq. yd.; thread count, 118 × 118) with the warp placed vertically in the tensile-testing machine. For purposes of comparison, there is included the load-extension curve for the material as tested in an ordinary one-dimensional grab test (curve *3*). It is believed that only curve *1*, showing the load against internal strain * as measured in the two-dimensional tester, has direct and useful significance. Curve *2*, the load against external strain as measured in the two-dimensional test, as well as curve *3*, the load against strain as measured in a one-dimensional test, are included to show that real differences exist between loads required to produce these various strains.

It will be noted in Figure 5 that the fabric appears stiffer in the two-dimensional test (curve *1*) than in the one-dimensional test (curve *3*). This increased stiffness reflects the cross-straining present in the two-dimensional stretching. It is believed that this actual stiffness under cross-straining may explain the premature failure of some fabrics that appear rather highly extensible under the conventional one-dimensional tests. Of course, much additional work will have to be done in order to test this conjecture.

To show some of the differences in the behavior of fabrics with respect to warp and filling directions of applied load, Figure 6 gives the ratio of warp load to filling load required to produce the same internal strain. As is to be expected, all of the fabrics tested (nylon, Orlon, cotton, Fortisan) have a greater stiffness in the warp direction than in the filling direction, the load ratio exceeding unity. However, the load ratio usually decreases as the strain increases. Of course, similar plots can be made on the basis of one-dimensional tests, but the results are not very regular, and it is believed that they are not likely to be meaningful.

Ultimately it will be desirable to know the behavior of fabrics not only under the same rate of strain in

* To obtain the internal strain in the two-dimensional test reported here, only one point of the strain-sensing device was used. The sensing point was placed 0.90 in. below the center of the sample, well within the homogeneously strained region (*cf.* Figure 3), and the internal strain in percent, ϵ, was computed from the observed deflection, δ, by the relation $\epsilon = (1.50E - \delta)/0.90$, where E is the external strain in percent.

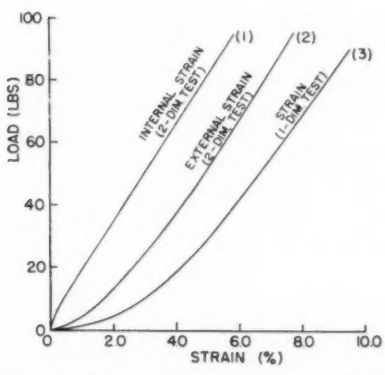

FIG. 5. *Load-extension curves for cotton fabric.*

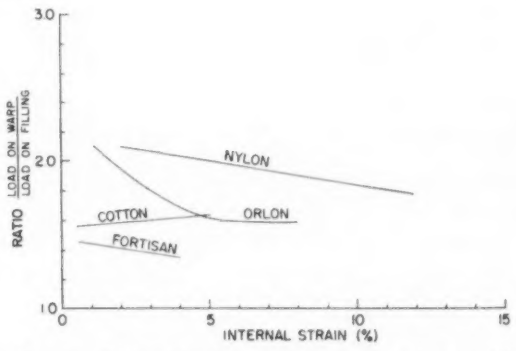

FIG. 6. *Ratio of load in warp direction to load in filling direction as a function of internal strain for four materials as studied in the two-dimensional tester.*

two perpendicular directions, but also under many other conditions of strain and load. It is hoped to map out the important regions by changing the angle of the wedges and the orientation of the samples in the jaws. Furthermore, it will be worth-while to study the connection between two-dimensional and one-dimensional results, in order to make use of the multitude of data available at present, and to permit reasonable estimates of fabric behavior on the basis of the simpler test. These problems are now under attack.

Acknowledgments

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Further Studies on Cotton Cellulose with Reduced Crystallinity*

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Abstract

Further studies have been made of the variables in the application of anhydrous ethylamine to cotton cellulose. The crystallinity of the product has been estimated by means of the acid-hydrolysis residue method. Indication of crystallite length has been obtained by the use of the "leveling-off" degree of polymerization. Reduction of crystallinity has been shown to take place rapidly and to be independent of the degree of polymerization of the cellulose. The maximum reduction in crystallinity was found to occur in material that was free of tension. Crystallite orientation was essentially unaffected by the treatment. The cellulose *II* pattern was always found in the cellulose after contact with mercerizing caustic, regardless of the sequence of treatment. A crystallite length of 150 anhydroglucose units seems to be a more stable structure after amine treatment than that of 225 units, which is usually found in native cotton.

In a previous paper [18] results of the treatment of cotton with ethylamine were reported which were interpreted as showing that a considerable reduction had taken place in the crystallinity of cotton cellulose. A number of implications of that work were left unexplored at that time.

Among these was the possibility that oxidative degradation, a process known to occur when cellulose is treated with aqueous alkaline reagents in the presence of air, could take place during the treatment with ethylamine. Also, there was some evidence presented in the previous paper which indi-

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cated that the effect of ethylamine in reducing crystallinity is a rapid one.

Although the ethylamine treatment acted on the crystalline areas to reduce the crystallinity without changing the type of crystal lattice, the previous data did not indicate what effect the treatment had on other parameters of the crystalline region. Thus, changes in crystallite orientation which might have an effect on tensile properties were not discussed. Neither was the increase in chemical reactivity of the material, which might be related to a decrease in crystallite size.

Crystallite size, which was not considered in the previous study, should have some degree of correlation with crystallinity; for instance, a smaller crystallite might be produced concurrently with the reduced crystallinity. Treatment with ethylamine while the cotton is kept under tension may prevent complete reaction, so that maximum decrystallization, and maximum effect on crystallite size, may not be realized. Nothing was known about how decrystallized cotton is affected by treating cotton with other chemical reagents either prior to or following the amine treatment.

The effect on cotton cellulose of amines other than monoethylamine was a matter worthy of consideration. Monoethylamine boils at 17°C, which necessitates the use of ice-baths and refrigeration in the treatment of material and in the storage and handling of the liquid amine. A higher-boiling amine capable of bringing about decrystallization would materially simplify the operations and equipment involved.

The work reported in the present paper is a continuation of the previous experiments. It was directed towards obtaining information which will help to clarify some of these problems in order that future data from chemical and physical testing of decrystallized cotton, and products prepared from it, may be evaluated properly.

Materials and Methods

The cellulosic materials investigated included (*a*) the commercially purified, cut cotton, described in the previous paper; (*b*) the kier-boiled, bleached, 20/1 loose-twist yarn, also described in the previous paper; (*c*) a card sliver; and (*d*) yarns made from seven different varieties of cotton.

Most of the experiments were carried out with anhydrous monoethylamine. However, the effect of diethyl-, triethyl-, and *n*-propylamines was also studied.

The experiments in which air was excluded from the samples were performed in a three-necked flask fitted with two stopcock connecting tubes which could be manipulated to evacuate the system and place it under an atmosphere of nitrogen. The system together with sample was purged of air by applying first vacuum and then nitrogen for a total of five cycles. The amine and then the chloroform, in the sequence required, were drawn into the system by application of vacuum; they were displaced by nitrogen. Proper precautions were taken at all times during the transference of the liquids to prevent air from being drawn into the system.

A few samples were mercerized with 18% sodium hydroxide at room temperature in the following way. The air-dry yarns, native and decrystallized, were immersed for 30 min., with the exclusion of air, after which the caustic was removed with distilled water. After a neutralization with 1% acetic acid and a final washing with distilled water, the samples were air-dried. When yarns were to be dried through solvent-exchange, the moist samples, after the final water wash, were transferred through several baths of dry methanol and then dry ether, followed by air-drying.

The crystallinities of the treated and untreated cottons were determined by the acid-hydrolysis residue method, as in the previous paper [18]. This method presents some difficulties when applied to low-crystallinity materials. Theoretically, if the recrystallization of amorphous cellulose, which has been discussed recently by Battista [2], should occur to any extent during hydrolysis, the crystallinity values will be too high. It is believed, however, that this does not greatly affect the determination because of the drastic conditions employed (6*N* HCl at 100°C). Experimentally, the acid-hydrolysis technique used here suffers the disadvantage that precision decreases as crystallinity decreases, because the straight-line portion of the log % residue *vs.* time curve is reached only at very low residue percentages. As a consequence, errors due to handling and weighing very small residues become proportionately greater, and long-range extrapolations, with attendant statistical uncertainty, must be performed.

The degree of polymerization of the treated and untreated materials was determined viscometrically by methods in use at this Laboratory [1, 4, 5, 20]. The cellulose was dispersed in cuprammonium hydroxide (concentration of dispersion, 0.5 g./dl.), and the intrinsic viscosity of the dispersion, given by the formula $[\eta] = 1.70\ (\eta_{sp})^{0.694} - 0.160$, was multiplied

TABLE I. THE EFFECT OF ATMOSPHERIC OXYGEN

Treatment	Degree of polymerization	"Leveling-off" D.P.	Crystallinity (%)
Purified cut cotton, untreated	1050	195	89
Overnight in ethylamine, under air	810	120	20
Kiered yarn, untreated	4680	230	90
4 hrs. in ethylamine, under air	3950	125	29
4 hrs. in ethylamine, under nitrogen	4550	120	26

by the factor 260 to obtain the degree of polymerization.

The determination of crystallite length by x-ray diffraction is a rather involved process, and for a first approximation a chemical method was used. It has been found by other workers [2, 3, 6, 7, 13, 16] that the degree of polymerization of hydrocelluloses * produced by moderate acid-hydrolysis approaches a constant value for the cellulosic material under study. This "leveling-off" degree of polymerization has been interpreted as being a function of the crystallite length [10, 11, 13, 15, 16], and in this light it was considered to be of great value in ascertaining the effect of ethylamine on crystallite size. In this study, the "leveling-off" D.P. was obtained by the method described by Nelson and Tripp [12]. Briefly, the material was hydrolyzed by hydrochloric acid under conditions which, on the basis of data obtained in the reference cited, would result in a hydrocellulose exhibiting the "leveling-off" D.P. In one or two cases, the adequacy of the hydrolytic conditions was verified by using different durations of hydrolysis in preparing the hydrocelluloses. Data obtained by this technique are open to the same consideration of recrystallization during hydrolysis as was the acid-hydrolysis crystallinity data. Battista's interpretation that crystallization of amorphous material occurs was based on observations made on material which was given a preliminary mild hydrolysis before being submitted to the usual drastic hydrolysis [2]. The conditions employed in the present study (2.5*N* HCl at 80°C) approximate his drastic hydrolytic conditions, under which only a minimum of crystallization would be expected.

Crystallite orientation of the fiber was determined by evaluation of the x-ray intensities around the 002 diffraction arc, according to the general method described by Sisson and Clark [19]. The distribution curves for the intensities from treated and untreated samples were obtained with a recording Geiger-counter x-ray spectrometer and a special rotating specimen mount [17]. The angular breadth of the intensity curve at half-maximum intensity [9] was taken directly from the chart.

X-ray diffraction patterns were obtained from ground samples, as in the previous paper [18].

Results

Effect of Atmospheric Oxygen

The earlier experiments with purified cut cotton and purified yarn were performed without regard to the exclusion of air. A consideration of the possibility of alkaline oxidative degradation made it necessary to show whether the reduction in crystallinity was independent of any change in the degree of polymerization.

The cut cotton which responded so well to the ethylamine treatment, although of high crystallinity, had already been considerably degraded as a result of its purification, as was shown by the relatively low degree of polymerization (1050 anhydroglucose units) as well as by the relatively short crystallite length ("leveling-off" D.P. of 195 units). When contact with air was allowed during the ethylamine treatment, a further degradation, amounting to 23% in D.P. value, occurred, as shown in Table I.

The untreated kiered yarn was shown to be normal in all respects. Although a smaller reduction in the degree of polymerization, amounting to 16%, was found after the amine treatment, the accompanying decreases in crystallite length and in crystallinity, as compared to those for the cut cotton, gave almost the same final values.

When the kiered yarn was treated with ethylamine while excluding air, the same crystallite length and the same reduction of crystallinity as in the previous samples were found. In this case, the degree of polymerization had decreased only 3% from that of the untreated yarn.

* In the "Report on Nomenclature in the Field of Macromolecules" (*J. Polymer Sci.* **8**, 257 (1952)), the term "partially hydrolyzed cellulose" is preferred. The term "hydrocellulose" is used here in view of current usage.

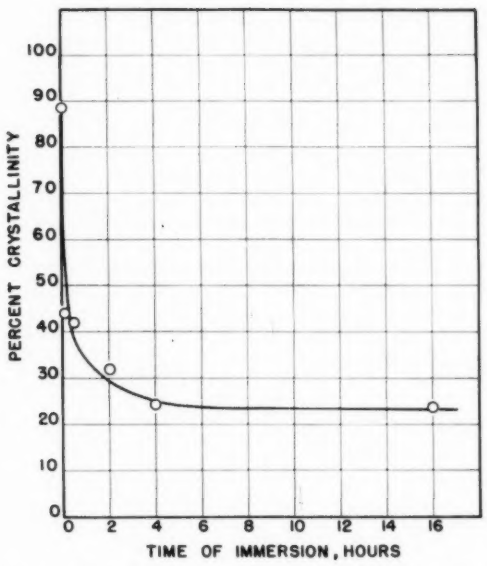

FIG. 1. *Crystallinity as affected by time of immersion in anhydrous ethylamine at ice-bath temperature.*

As a result of these findings, subsequent work was carried out with the exclusion of air in the manner described.

Effect of Immersion Time

Although some evidence was found in the experiments of the previous paper to show that the length of time the cotton was immersed in the ethylamine had some effect on the extent of decrystallization, experiments at ice-bath temperature indicated that 70% of the maximum reduction had been realized after an immersion time of only 5 min. (Figure 1). This indicated that the effect of ethylamine, like that of mercerizing caustic, is a rapid one. In the subsequent preparations of decrystallized cotton, however, a 4-hr. immersion in ethylamine was used since the data indicated that some further reduction was achieved up to this time.

Relation between Crystallite Length and Crystallinity

In Table I it can be seen that the reduced crystallinity was accompanied by a fairly consistent reduction of crystallite length ("leveling-off" D.P.).

The apparent correlation between the crystallite length and the crystallinity was given much consideration as a possible means of circumventing the rather tedious and lengthy acid-hydrolysis method of determining crystallinity, which is prone to considerable experimental error, especially as the crystallinity is lowered. The determination of crystallite length can be done fairly rapidly and with greater precision.

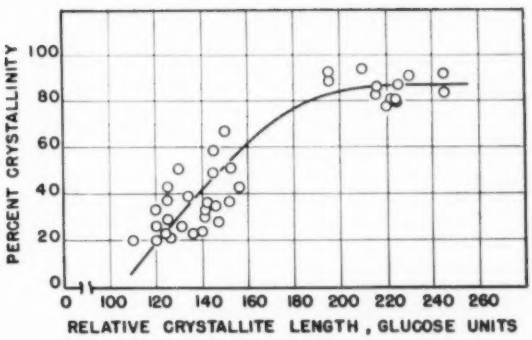

FIG. 2. *The relation between crystallite length and crystallinity.*

When the data from a large number of samples were assembled, and the crystallinities were plotted against crystallite length (Figure 2), the relationship did not show sufficiently close correlation so that crystallinity could be read from the crystallite length value on a chart. The data, however, became useful from another standpoint. It was noteworthy that the "leveling-off" D.P. values (crystallite length) obtained on a number of samples which had received similar treatments were remarkably constant. This seemed to indicate that the trend existing in the plot of Figure 2 might be useful for grouping the results according to treatment. Some typical data are given in Table II which illustrate the association of crystallite length with type of treatment.

The Use of Amines Other than Monoethylamine

In the previous study [17] ethylamine, hexylamine, and heptylamine had been studied. Of these, only

TABLE II. VARIATION IN CRYSTALLITE LENGTH WITH MANNER OF TREATMENT

Treatment	"Leveling-off" D.P.	Crystallinity (%)
Untreated kiered yarn	230	90
Untreated raw yarn	224	80
Decrystallized kiered yarn	120	26
Decrystallized raw yarn	124	23
Decrystallized yarn after 2-hr. water-boil	145	59
Decrystallized yarn after 2-hr. water-boil	145*	—
Mercerized yarn, without tension	150	72

* Duplicate of sample immediately above.

TABLE III. CRYSTALLINITIES RESULTING FROM TREATMENT WITH AMINES OTHER THAN ETHYLAMINE

Amine used	Basic ionization constant K_b	Crystallinity (%) Treated at ice-bath temperature	Crystallinity (%) Treated at room temperature
n-propylamine	4.7×10^{-4}	40	86
diethylamine	1.3×10^{-3}	87	87
triethylamine	6.4×10^{-4}	84	87

TABLE IV. CRYSTALLITE ORIENTATION OF NATIVE AND DECRYSTALLIZED COTTONS AS SHOWN BY X-RAYS

Material	Orientation (degrees)	Crystallinity (%)
Untreated kiered yarn	29.3 ± .2	90
Decrystallized yarn	29.4 ± .2	29
Untreated raw card sliver	27.8 ± .3	84
Decrystallized sliver	27.6 ± .1	24

TABLE V. CRYSTALLITE LENGTHS RESULTING FROM TREATMENTS INVOLVING SODIUM HYDROXIDE AND ETHYLAMINE

Sequence of treatments applied to yarns	"Leveling-off" D.P.
Untreated control	230
Amine-treated only	120
Mercerized, then amine-treated	140
Amine-treated, then mercerized	150
Mercerized, dried through solvent-exchange	150
Amine-treated, then mercerized, dried through solvent-exchange	150

ethylamine was found to be effective in reducing crystallinity. Hexylamine and heptylamine by themselves were ineffective. The rather special property of ethylamine in this respect has been confirmed by extending the study to include several other anhydrous amines, the data for which are given in Table III.

Whereas ethylamine had been shown to be effective at both room and reduced temperatures, *n*-propylamine was found to have less effect and this only at reduced temperature. This effect is similar to one observed in mercerization, where the temperature has to be kept below a certain level. The reduced crystallinity obtained with propylamine at ice-bath temperature was confirmed by the crystallite length of 156 and by the changed intensities in the x-ray diffraction pattern.

Diethyl- and triethylamines were ineffective in reducing crystallinity. Triethylamine, not having the linear configuration of the primary amine, and diethylamine, approximating that configuration but with the nitrogen atom centrally located, introduce the factor of structural configuration.

When treatments with diethyl- and triethylamines were preceded by treatment with ethylamine, as was done in the previous paper with hexyl- and heptylamines [17], reduction in crystallinity was obtained which was the same as that obtained with ethylamine alone. The resulting crystallite lengths were 120 and 130, respectively. When *n*-hexylamine was used in this manner, a value of 125 was found. These data again indicated that ethylamine, of all the amines studied, has the greatest effect on the cellulose.

The Orientation of the Crystallites

The far-reaching effect of ethylamine on the extent of the crystalline regions of cotton cellulose has been demonstrated by chemical means. X-ray diffraction, while qualitatively confirming the chemical results, has shown that the crystal lattice of the treated cotton remains that of cellulose *I*. Since in the treated cotton the crystalline regions exhibit a change in extent, but not in lattice type, there remains the possibility that the orientation of these regions with respect to the fiber axis might change. This change would be expected if any appreciable change in fiber diameter occurred. However, when native and decrystallized cottons were examined, the orientation, as given by the "half-maximum angle," was found to be essentially unchanged. Typical data are given in Table IV. The difference in orientation for the two untreated cottons is much less than the range ordinarily found among native cottons.

Treatments with Sodium Hydroxide in Conjunction with Ethylamine

Whereas ethylamine, applied in the manner already described, brings about a great reduction in crystallinity with no change in the type of crystal lattice, sodium hydroxide in the process of mercerization causes only a moderate reduction in crystallinity accompanied by a shift in lattice type from cellulose *I* to cellulose *II*. Conjecture as to the effect of ethylamine on mercerized cotton led to an interesting series of experiments, some results of which are presented in Table V.

The crystallite length of 150 units obtained for the amine-treated mercerized cotton indicates that there

TABLE VI. THE EFFECT OF TENSION ON THE YARN DURING AMINE TREATMENT

Sample	Crystallinity (%)			"Leveling-off" D.P.		
		Treated			Treated	
	Untreated	Without tension	With tension	Untreated	Without tension	With tension
Sample A	78	21	33	220	126	141
Sample B	83	23	37	215	124	152
Sample C	67	26	35	226	131	146
Sample D	81	30	43	224	141	156

was little difference between it and ordinary mercerized cotton.

Drying the wet mercerized cottons by the solvent-exchange technique, in order to retain the maximum reduction in crystallinity which might be realized, did not improve the results obtained by the usual mercerizing process. The data given in Table V show that the crystallite length was the same as that obtained by any of the other variations in the treatments.

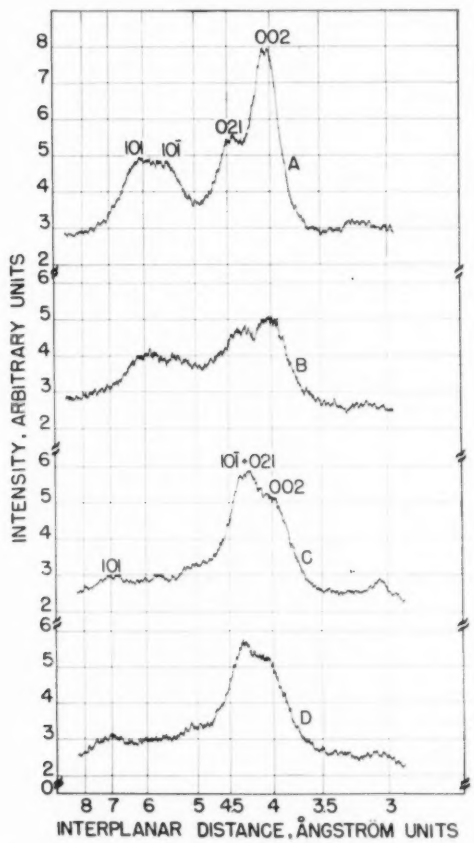

FIG. 3. *Radial traces of diffraction intensities along the equators of the x-ray patterns of cottons treated with ethylamine and sodium hydroxide.* A—*Untreated cotton.* B—*Decrystallized cotton (amine-treated).* C—*Amine-treated cotton after mercerization.* D—*Mercerized cotton after amine treatment.*

In the x-ray diffraction investigation of those samples where sodium hydroxide had been used, cellulose *II* patterns were found in all cases with almost equal relative intensities (Figure 3). This qualitative indication of similar degrees of crystallinity supported the chemical evidence discussed above.

The Effect of Tension on the Yarn during Treatment

In carrying out the experiments discussed above, for convenience in handling, yarns have been treated batchwise in the loose state. Philipp and coworkers [14] had found that yarn mercerized in a loose condition had a crystallinity of 67%, but 78% when the yarn was mercerized under maximum tension. These data would lead one to wonder if a similar effect would be observed for the amine treatment.

To test this, several yarns were treated with ethylamine. In one set, skeins were treated loose or in the relaxed state; in a second set, skeins were held to constant length during treatment by being wound on a jig. Thus, no shrinkage in length could occur during the treatment. No treatment was applied to a third (control) set. Some results from these experiments are given in Table VI. In each case where a higher crystallinity resulted, a greater crystallite length accompanied it. Where tension was present the crystallinities ranged from 9%–14% higher, and the crystallites 15–28 units longer than where the treatment was applied to yarns in the relaxed state. It is apparent from these data that tension in the yarn does limit the effect of the ethylamine treatment.

Discussion

From these experiments emerge several significant findings concerning the application of ethyl-

amine in the decrystallization of cotton cellulose. Degradation of the cellulose was shown to be avoided by the exclusion of air during the amine treatment. This permits retention of tensile strength in the fiber, which would otherwise be weakened as the degree of polymerization is lowered by alkaline oxidation. The effectiveness of the reagent in attacking the crystalline regions of the cellulose, as indicated by the acid-hydrolysis data, appeared to be independent of the degree of polymerization.

Since the length of time that cotton is immersed in the reagent influences the extent of the reduction of crystallinity, a way is provided for controlling the degree of crystallinity of cotton, but the usefulness of this has not yet been explored. The rapidity with which decrystallization occurs has practical implications—for example, in making possible the utilization of the process in a continuous operation involving cotton yarns or cords.

A decrease in crystallite length may be explained on the basis that ethylamine penetrates the crystalline region endwise, thus causing chain separation and distention to occur at the ends of the region. If the amine proceeds from a transitional zone between the amorphous and the crystalline regions, entering the crystalline area along the cellulose chains, separation of the chains would proceed until stopped by the combination of high order deep in the crystalline region and the release of chain tensions. The resulting distended ends of the crystalline region would not be expected to exhibit crystal order, but should show amorphous reactivity. The remaining crystalline area would then effectively possess a shorter length.

The reduction of crystallinity as a result of the amine treatment is accompanied by a decrease in crystallite length (Table I and Figure 2), which is consistently observed. These findings are supported by a similar indication of reduced crystallite length which was found by Heyn [8], using a small-angle x-ray scattering technique on ethylamine-treated cottons furnished by this Laboratory.

Crystallite length seems to be a property that is fairly sensitive to variations in treatment, and in the low crystalline region seems to be a more reliable guide to reduced crystallinity than is the acid-hydrolysis method itself.

There are indications that after amine treatment a crystallite length of about 150 anhydroglucose units is the more stable unit existing in cotton. This was found, for example, in cotton yarns held to constant length (Table VI), as well as in those resulting from the application of other modifications of the treatment to cotton. After decrystallized cotton is boiled for 2 hrs. in water, the crystallite length of cotton is found to have increased from about 120 units to about 150 units (Table II). The data in Table V seem to indicate that a crystallite length of 150 units is characteristic of the mercerization treatment, and when *n*-propylamine is applied at ice-bath temperature, a similar value is obtained. Further studies are being made on this effect.

In attempting to explain the differences in action of the amines on the crystallinity of cellulose, factors other than the steric one were examined. The ionization constants of the amines do not suggest basicity as a contributory factor. Thus, the value of this constant for monoethylamine is 5.6×10^{-4} which lies well in the range covered by the other amines (Table III). Although the ionization constants of the organic bases might be related to the degree of hydrogen-bonding in them, ionization of the bases would not be a factor since in all cases the anhydrous liquids were used.

The more probable cause of the observed effects may be the capabilities of the amines for forming hydrogen bonds. There may be variations in the bond-forming tendencies between associated amine molecules and between amine and cellulose molecules, but the manner in which this might operate is not yet clear.

The results obtained in the experiments with strong sodium hydroxide and ethylamine were unexpected in that the cellulose *II* crystal pattern typical of mercerization always predominated over the cellulose *I* crystal pattern typical of the application of ethylamine. This always followed, regardless of the sequence of application of the reagents. This is important since it means that any advantages gained by the amine treatment would be lost in further processing where sodium hydroxide of mercerizing strength or stronger is used.

Summary and Conclusions

An extended study has been made of the variables in the application of ethylamine to cotton cellulose which may have some effect on the final reduced crystallinity. The crystallinity of the products has been estimated by the acid-hydrolysis residue method. The indication of the crystallite length has been ob-

tained through the determination of the "leveling-off" degree of polymerization. The following conclusions were made from this study:

Exclusion of air during the processing minimizes the possible degradation resulting presumably from alkaline oxidation. Exclusion is important in order to retain tensile strength. Reduction of crystallinity is independent of the degree of polymerization of the cellulose.

The reduction in crystallinity is brought about rapidly, with most of the change occurring in the first 5 min. and the maximum effect in about 4 hrs. Accompanying the decrease in crystallinity is a decrease in the crystallite length.

The orientation of the crystallites with respect to the fiber axis is unaffected by the ethylamine treatment.

Contact with sodium hydroxide solutions of mercerizing strength, either before or after treatment with ethylamine, results in mercerized cotton, with the typical cellulose *II* diffraction pattern. This limits the utilization of decrystallized cotton to processes that do not use caustic solutions of mercerizing strength.

The maximum reduction in crystallinity and crystallite length can be realized by keeping the cotton in a loose or relaxed condition. When the yarn is held to a constant length during the treatment, thus allowing the tension to build up, the resulting crystallinity and crystallite length are both found to be greater.

A crystallite length of about 150 glucose units seems to be the more stable structural unit for the cellulose *I* lattice existing in cotton following the amine treatment.

Acknowledgment

Appreciation is expressed to Miss H. M. Ziifle for the computations and the drawings, to Mr. J. J. Creely for the x-ray diffraction recordings, and to Mr. Trinidad Mares for the viscometric determinations.

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(*Manuscript received December 12, 1952.*)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Effects of Ultrasonic Radiation on the Viscosity of Cellulose Solutions

TEXTILE RESEARCH INSTITUTE
Princeton, New Jersey
March 3, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The depolymerizing effects of ultrasonic radiation on certain polymer-solvent systems have been reported by many authors over the past fifteen years [1, 2, 4–9]. A primary cause for the degradation of polymers in solution by ultrasonic waves is believed to be "cavitation," which has been defined as "the formation and violent collapse of small bubbles or voids in the liquid as a result of pressure changes which occur, for example, in a sound wave" [9]. The degree of such degradation depends, among other things, on the D. P. of the polymer, the concentration of the solution, and the field intensity of the ultrasonic radiation. It has been implied in the literature that inter- and intramolecular bonds may be attacked selectively [4, 5].

We have recently conducted some preliminary experiments on a system which, to the best of our knowledge, has not been previously reported in the literature. The results, although fragmentary and inconclusive, are deemed of sufficient interest to warrant this communication.

Samples of bale and grey yarn from a single cotton variety (Stoneville 2B) and samples of bright viscose rayon were dissolved in 0.5*M* cupriethylenediamine. Their solutions were protected from oxidative degradation by nitrogen which was purified by passage through an alkaline pyrogallol column [10]. Portions of each solution were then exposed to ultrasonic radiation for periods of time not in excess of 5 min., at a frequency of 400 kilocycles/sec. at a power output of 250 watts. Viscosity measurements were used to estimate the degradative effects of the treatments.

The irradiated solutions of the cotton samples showed a marked decrease in viscosity, while similarly treated solutions of viscose rayon samples were entirely unaffected. No effort was made to control cavitation in either case. The original differences between the bale and yarn cotton samples, which have been characterized as being due to mechanical-processing degradation [3, 10], appeared to have been retained after irradiation. All solutions were stored under nitrogen and tested at intervals over a period of 3 weeks; no recovery in viscosity was observed during this period. From this result it is concluded that the viscosity decrease resulting from irradiation is, in this instance, primarily associated with the rupture of valence bonds. The results on viscose rayon when compared with those on cotton may indicate basic differences in the solutions other than D. P. differences.

Further work with ultrasonics seems a logical approach to the study of fundamental questions concerning the nature of cellulose dispersions in cuprianine bases.

The writers are indebted to Burlingame Associates for the loan of a Brush Hypersonic Generator (Model BU-204).

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R. F. SCHWENKER, JR.
J. C. WHITWELL

The Determination of Nep Counts

THE BRITISH RAYON RESEARCH ASSOCIATION
Manchester, England
February 12, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In his paper "The Determination of Nep Count in Tops" (*J. Textile Inst.* **42**, No. 2, P81–5 (Feb. 1951)), F. Monfort points out that the nep count of wool tops follows the statistical Poisson law.

It can be shown that on the basis of very simple and obvious assumptions, which evidently are applicable to tops, this law can be derived. This derivation elucidates to some extent the occurrence of nep formation and, moreover, may give a clue to causes of nep formation if, which could conceivably happen, a nep count obtained in practice deviates significantly from Poisson's law.

The fundamental assumption consists in taking the probability of a single nep being found in an infinitely short length δs of the top sliver being proportional to this length δs, say $\alpha\delta s$, the probability of an occurrence of more than one nep being of higher order in δs. It is also assumed that the probability at any one point is independent of the number of neps before and behind the place under consideration. The following deviation is similar to others occurring in statistics—notably in time series. If, then, we call $p_n(s)$ the probability of finding just n neps in a length s of the sliver, the following differential equation must hold:

$$p_n(s + \delta s) = p_{n-1}(s)\alpha\delta s + p_n(s)(1 - \alpha\delta s), \quad (1)$$

where $n = 0, 1, 2 \ldots \infty$. This means that the probability of finding just n neps in a length $s + \delta s$ of top sliver (δs being infinitely small) is equal to the sum of the probability of finding $n - 1$ neps in the length s and one in the short length δs, and the probability of finding n neps in the length s and none in δs. From the significance of the p_n it will be seen that equation (1) also hold for $n = 0$ if we take $p_{-1}(s)$ to be zero by definition. The initial condition is that no neps occur in a piece of top sliver of length o—*i.e.*,

$$p_0(0) = 1, \quad p_n(0) = 0, \quad n = 1, 2 \ldots . \quad (2)$$

Equation (1) forms a system of infinitely many ordinary differential equations of first order for the functions p_0, p_1, etc. Their solution is appreciably simplified by introducing the probability generating function

$$G(t, s) = \sum_0^\infty t^n p_n(s). \quad (3)$$

In view of equation (1) we then obtain

$$\begin{aligned} G(t, s + \delta s) &= \sum_0^\infty p_n(s + \delta s)t^n \\ &= \alpha\delta s \sum_1^\infty p_{n-1}(s)t^n \\ &\quad + (1 - \alpha\delta s) \sum_0^\infty p_n(s)t^n \\ &= (1 - \alpha\delta s + t\alpha\delta s)G(t, s), \end{aligned} \quad (4)$$

or, developing the left side and dividing by δs,

$$\frac{\partial G}{\partial s} = \alpha(t - 1)G. \quad (5)$$

The initial condition for G is

$$G(t, 0) = 1, \quad (6)$$

which follows from equations (3) and (2).

The solution of equation (5) then becomes

$$G(t, s) = e^{\alpha s(t-1)} = e^{-\alpha s} \sum_{0}^{\infty} \frac{(\alpha s)^n}{n!} t^n. \qquad (7)$$

Comparing this with equation (3), it is seen that

$$p_n(s) = \frac{(\alpha s)^n}{n!} e^{-\alpha s}, \qquad (8)$$

which is Poisson's law, with $\alpha s = m$ as mean and variance.

It is clear, therefore, that in a case where the nep count does *not* obey Poisson's law, the above assumptions are not applicable. This may, for instance, be the case if α depends on s—e.g., because the number of neps at any particular point is affected by the number of neps in its neighborhood—or if α is not constant—*e.g.*, if the quality of the sliver varies—or, finally, if the tow is so bad—*i.e.*, the nep content so high—that the probability of having more than one nep in an infinitely short piece of sliver can no longer be neglected as being of higher than first order $n\delta s$.

In all such cases further statistical investigations are required, and may lead to practical suggestions for improvement.

K. K. SCHILLER

The Shearing of Filaments and Yarns

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts
February 14, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

As the study of textile mechanics advances, we may expect that increased attention will be given to the resistance of the individual fiber to shearing stresses. In the past, the textile technologist has evaluated the modulus of shear rigidity by means of the fiber torsion pendulum, or similar twisting devices. In one instance [1], a special cutting device was developed for the measurement of the "shear strength" of filaments and fibers. The results of experiments with this mechanism showed characteristic *relative* variations among the "shear strengths" of different fibers. But the *absolute* level of the "shear strength" is not only dependent on the type of material which is cut, but on the geometry of the cutting surfaces as well. As pointed out in a previous paper [2], the horizontal force required to push a tool through an isotropic crystalline solid is dependent on the rake angle of the cutting edge and the depth of cut. The Merchant derivation, to which reference was made, indicates the added importance of friction between the material being cut and the tool face.

We have attempted to apply the theories of metal cutting to textile materials. The first step was to cut blocks of solid plastics (without external lubricants) and measure the forces on the tool for various rake angles and depths of cut. The forces and geometric dimensions measured were observed to follow closely the relationships which govern the metal-cutting process.

The measurement of forces necessary to cut fibers presents a more difficult problem in instrumentation because of the smaller specimen size. Our experiments have accordingly been limited to microscopic observation of the cutting action which occurs in shearing tests, such as those carried out by Finlayson [1]. We believe that the typical cases we have observed will be of general interest, and the purpose of this letter is to furnish a few sample photomicrographs.

We have built a microscope stage compressor in which movement of a microcompression or cutting jaw in the microscope field on view may be controlled. The filament or yarn being cut is held in a pair of fixed flat jaws at a point outside the field of view. The free end of the specimen extends along the inner face of the longer of the two jaws. The top of this jaw is carefully machined, perpendicular to the jaw face. The plan view of this right-angle edge is visible in the lower right-hand quadrant of the field of view. The edge of the cutting jaw is moved from left to right, horizontally across the field of view so as to shear off all material which projects beyond the top edge of the fixed jaw. The right-angled cutting edge is visible in the upper left quadrant.

Figure 1 illustrates the chip formed in cutting off the top of a 50-mil polyethylene monofilament. During the cutting operation, a chip of the filament is formed, which rides up the face of the cutting edge and finally curls in much the same manner in which a metal chip behaves at the face of the tool. Similar action is observed in the cutting of a woolen yarn (Figure 2), although in this case each fiber acts separately, and after being cut is forced up the tool face in a manner resembling the chip action of Figure 1. Figure 2 was, in fact, taken after part of the yarn had been cut and the tool partially withdrawn, allowing slight recovery of the uncut portion.

When the specimen is not clamped in the fixed jaws, the cutting action causes it to rotate between the top edge of the longer fixed jaw and the bottom edge of the moving cutter jaw. Under these conditions, a double-wedging or cutting action results, such as is pictured in Figure 3 for a 10-mil polystyrene monofilament. It is evident from these photographs that the nature of the cutting action will depend on the geometry of the cutting surfaces and the rigidity of the specimen between the cutting edges. It is further noted that the destructive shearing action of the cutting blade is not simultaneous over the entire cross section of the specimen; it is, instead, a progressive shearing similar to that observed when a tool cuts isotropic metals or orthotropic woods. It follows that the maximum horizontal shearing force (per unit length of active cutting edge) required to sever a fibrous mass should be the same whether we are cutting 20,000-den. or 50,000-den. bundles. However, an increase in the volume of fiber to be cut will, after the initial flattening of the bundle, effectively increase the length of active cutting surface, and simultaneously increase the total "shear force" required in cutting. Depending upon the shape of the fiber mass compressed between the jaws, the length of the effective cutting edge may vary during a given shear test. Such a variation poses a distinct problem in determining the effective blade length, for this is the dimension which one needs for calculation of the inherent average cutting resistance of the fibrous material. Another factor which warrants further investigation is the fact that an increase of sample size in a cutting test will also alter the magnitude of the frictional resistance of the freshly cut surfaces against the moving blade.

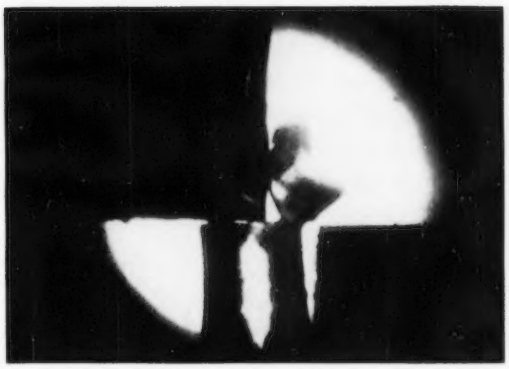

FIG. 1

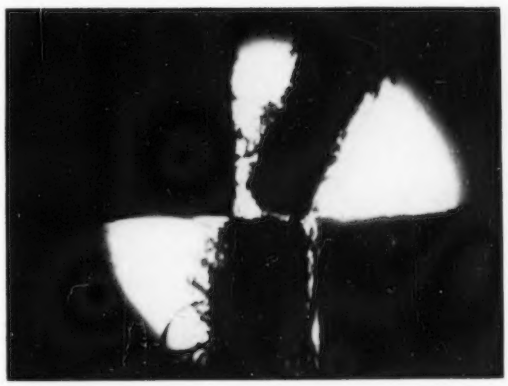

FIG. 2

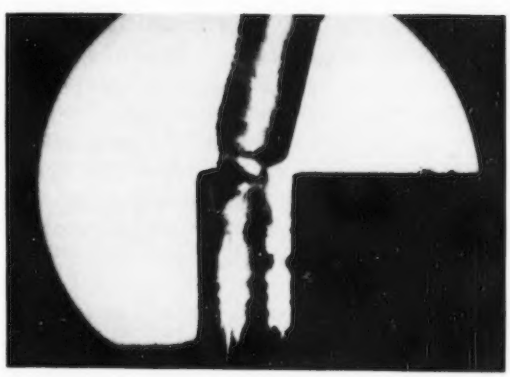

FIG. 3

The measurement of the "shear strength" of textile fibers is a problem presenting interesting complexities. Their investigation should be worth-while in view of their practical implications in the manu-

facture of spun synthetics and in the finishing of woven and knitted fabrics. If this does not provide sufficient incentive, the study of fiber cutting should win the support at least of the male element of our population, which, with the exception of the bearded contingent, personally performs this experiment daily.

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The Allwörden Reaction

INSTITUT TEXTILE DE FRANCE
Paris, France
March 4, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In their article "A New Method of Producing the Allwörden Reaction," Mercer and Golden [1] described the formation on wool treated with peracetic acid of bubbles analagous to those obtained by halogen solutions. They observed a "coalescence" of bubbles, which proves the continuity of the epicuticular membrane. Their micrographs suggest definitely a local lifting of a continuous membrane forming a sheath around the fiber. However, we do not agree with these authors on the interpretation of the phenomenon. In our opinion, it is very probable that the membrane, which limits the bubbles formed under these conditions, consists not of the epicuticle of Müller-Lindberg, but of the entire cuticle, which is also capable of playing the role of a semipermeable membrane, as we have shown recently [2]. In their first photograph, one can distinguish on certain bubbles traces of scale edges, which would appear probably much more clearly when placed in favorable optical conditions—for example, in phase-contrast. On the other hand, the apparent thickness of the membrane is considerable (of the order of μ), so that the contours of the bubbles are perfectly clear, whereas the bubbles of the epicuticle proper are usually scarcely visible on a bright background.

For the purpose of comparison, three photomicrographs of hairs from the Siamese cat are shown here: the first represents a hair treated with chlorine water (Figure 1); the two others, hairs treated with bromine water, the focus for the one being on the surface of the bubbles (Figure 2) and for the other on their profile (Figure 3). It is clear that the chlorine water has raised a very fine membrane, which is the genuine epicuticle, while the bromine water has raised a much thicker membrane formed of scales, which is no other than the cuticle. The three photomicrographs were taken by means of phase-contrast at a magnification of 600.

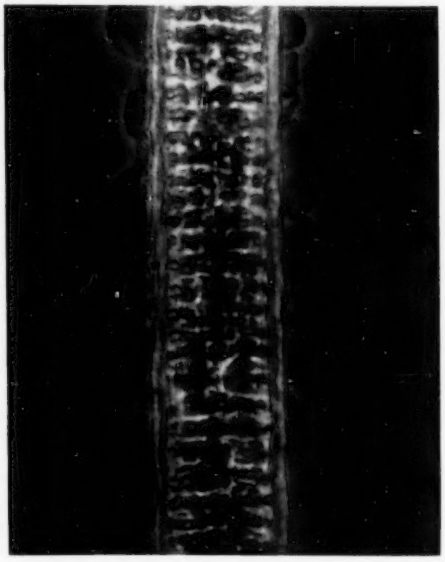

FIG. 1. *Hair (from Siamese cat) treated with chlorine water. The bubbles are limited to the epicuticle.*

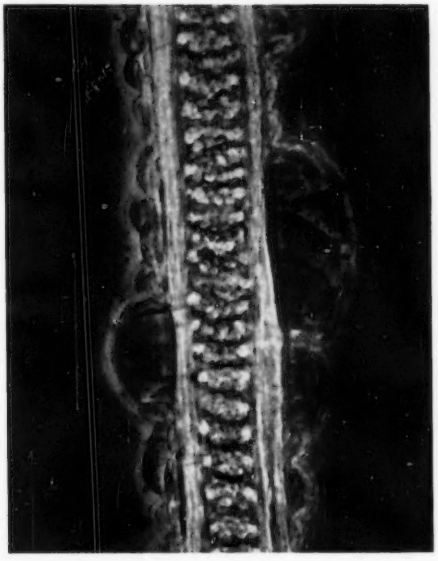

FIG. 2. *Hair (from Siamese cat) treated with bromine water. The bubbles are limited to the cuticle. The focus is on the surface of the bubbles.*

FIG. 3. *Hair (from Siamese cat) treated with bromine water. The bubbles are limited to the cuticle. The focus is on the profile of the bubbles.*

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A. PARISOT
M. LEVEAU

Authors' Comments

In the above letter, and in their previous article [2], the writers have emphasized certain peculiarities of the Allwörden reaction which have been observed by us and which were also described by Müller in his very detailed study of the reaction. The thickness of the membrane which forms the walls of the Allwörden bubbles is very variable, depending on the treatment used to provoke bubble formation and on the type of hair used. These differences are even more obvious when the membranes are examined by means of the electron-microscope. In all cases, however, the membranes may be described as epicuticle thickened by more or less of the adhering protein of the cuticular cells [1]; but when the cuticular adhesions become the dominant constituent, then one may say appropriately that the cuticle itself has lifted off as a whole. Accordingly, we find ourselves in good agreement with Leveau and Parisot. The problem of the chemical or histological reasons for the different types of Allwörden reaction remains, and is in need of further investigation.

E. H. MERCER
R. L. GOLDEN
Textile Research Institute
Princeton, N. J.

(March 20, 1953.)

Book Reviews

Physiology of the Fungi. Virgil G. Lilly and Horace L. Barnett. New York, McGraw-Hill Book Co., Inc., 1951. 464 + xii pages. Price, $7.50.

(Reviewed by Edward Abrams, Southern Research Institute, Birmingham, Ala.)

This is an entirely new book in the well-documented field of the fungi. The authors are eminently qualified in their field.

Stimulated by the rapid development of industrial microbiology and antibiotics, the volume of literature in these fields has increased greatly. From this point of view, the authors have developed a textbook of the physiology of the fungi which is helpful in cultivating fungi and in evaluating the results of their growth. This volume will be equally useful as a reference book in the industrial laboratory.

In the first part of the book, the purely physiological aspects of the fungi are discussed. The items discussed include culture media, growth, enzymes and enzyme action, essential metallic and nonmetallic elements, carbon sources and carbon utilization, pH, and vitamins and growth factors. The use of fungi as test organisms is described. Fungi are used to assay vitamins, amino acids, and other biologically active materials. Also, they are important to the textile industry because they are used to test fabric protectants. Although this subject is only mentioned briefly, the list of references given is complete and up to date.

One chapter is concerned with the action of fungicides. Although the whole field of protectants is labeled "fungicides," the authors distinguish between a fungicide and a fungistat. A fungistat is a protectant that either completely or partially inhibits one of the life processes of a fungus. However, this inhibition may be reversed. On the other hand, a fungicide causes death. The authors also recognize the fact that a fungistat may become fungicidal if the concentration is increased or the time of exposure is lengthened.

The remaining chapters are concerned with the metabolic products of fungi, factors affecting sporulation, spore germination, and physiological variation, and inheritance of physiological characters.

This book will be a welcome addition to the library of the textile microbiologist. Especially valuable are the lists of suggested readings and references at the end of each chapter.

Wasser und Abwasser in der Textilindustrie (Water and Waste Water in the Textile Industry). M. Kehren. Basel, Switzerland, Schweizerischen Vereinigung von Färbereifachleuten, 1951. 206 pages. Price, $3.00 + postage.

(Reviewed by Edward Abrams, Southern Research Institute, Birmingham, Ala.)

This book is noteworthy because it is one of the relatively few books which is devoted entirely to the water problems of the textile industry. Unfortunately, it is in German and thus will be available to only a small number of those who might otherwise benefit from it.

The book is divided into seven parts as follows: physical and chemical properties of water; industrial water; the requirements for the quality of industrial water for use by the textile industry; purification of industrial water for textile uses; removal of salts causing hardness; textile waste water and its purification; methods of water examination.

The author discusses, under the heading "Industrial Water," rainwater, condenser water, surface water, and ground water. In the chapter devoted to quality of water, the requirements are listed for the following operations: boiler feeding, bleaching, piece goods washing and soap processing in dyeing and printing, washing of white goods, dyeing and manufacture of synthetic fibers.

In the chapter on the purification of water for textile use, the following methods are discussed: filtration and clarification of surface water, deacidification and decarbonization, degassing, removal of oil from condensate, removal of iron and manganese, water softening by various methods, and removal of silica from boiler feed water.

For those who can read German, this is a worthwhile book.

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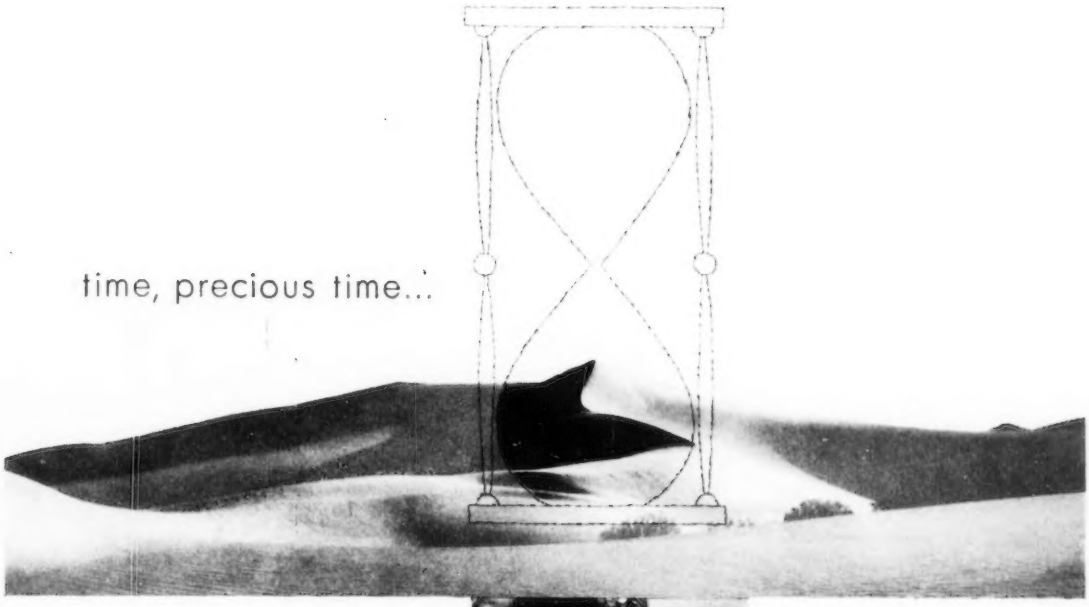

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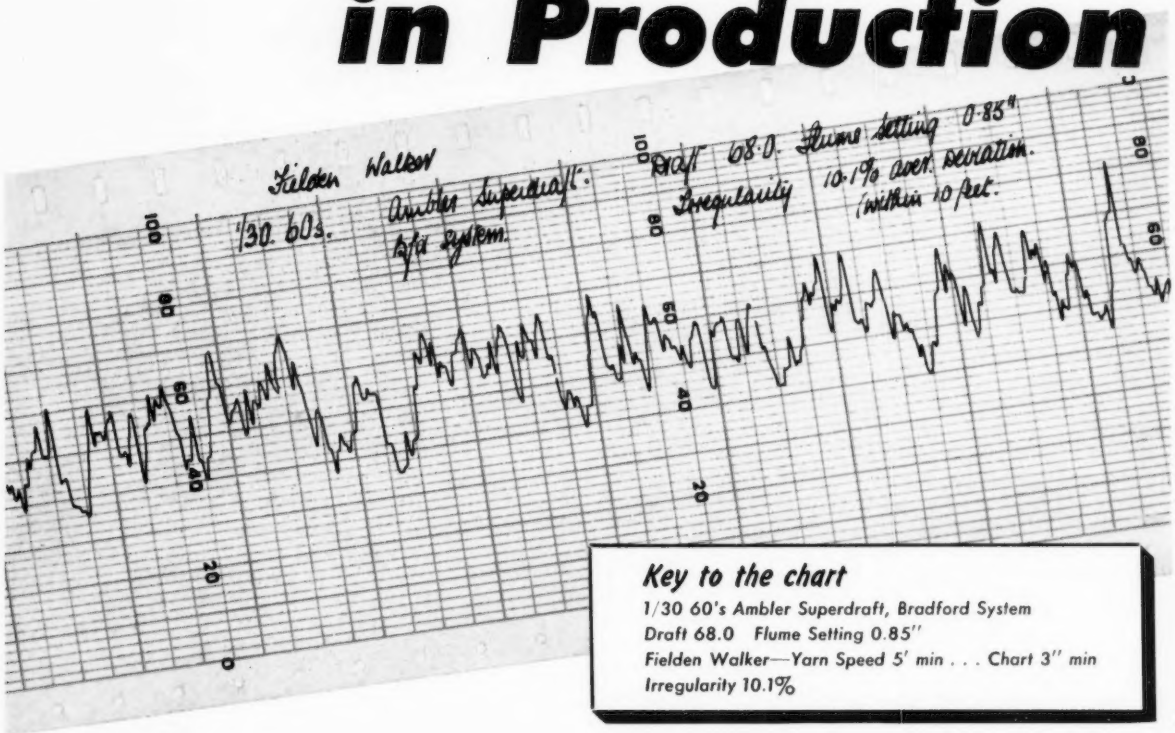

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